

10089975-440802  
JC05 Rec'd 03/17/00 08 APR 2002

FORM PTO-1390  
(REV 10-95)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

**TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. §371**

MERCK 2405

U.S. APPLICATION NO. (If known, see 37 CFR §1.5)

**10/089975**

INTERNATIONAL APPLICATION NO.

PCT/EP00/09133

INTERNATIONAL FILING DATE

18 SEPTEMBER 2000

PRIORITY DATE CLAIMED

6 OCTOBER 1999

TITLE OF INVENTION

LIQUID-CRYSTALLINE PHENOL ESTERS

APPLICANT(S) FOR DO/EO/US

REIFFENRATH, Volker, et al

**Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:**

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. §371
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. §371.
3. ☐ This express request to begin national examination procedures (35 U.S.C. §371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. §371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19<sup>th</sup> month from the earliest claimed priority date
5. ☒ A copy of the International Application as filed (35 U.S.C. §371(c)(2))
  - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☒ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ A translation of the International Application into English (35 U.S.C. §371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. §371(c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. §371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. §371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. §371(c)(5))

**Items 11. to 16. below concern document(s) or information included:**

11. ☐ An Information Disclosure Statement under 37 C.F.R. §§1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 C.F.R. §§3.28 and 3.31 is included
13. ☒ A **FIRST** preliminary amendment.
 ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☐ A substitute specification
15. ☐ A change of power of attorney and/or address letter.
16. ☐ Other items or information:


U.S. APPLICATION NO (if known, see 37 CFR §1.5) <b>10/089975</b>	INTERNATIONAL APPLICATION NO. PCT/EP00/09133	ATTORNEY'S DOCKET NUMBER MERCK 2405
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17. <input checked="" type="checkbox"/> The following fees are submitted:				<b>CALCULATIONS</b> PTO USE ONLY	
<b>BASIC NATIONAL FEE ( 37 CFR §1.492 (a) (1) - (5)):</b>					
Search Report has been prepared by the EPO or JPO.....				\$890.00	
International preliminary examination fee paid to USPTO (37 CFR §1.482).....				\$710.00	
No international preliminary examination fee paid to USPTO (37 CFR §1.482) but international search fee paid to USPTO (37 CFR §1.445(a)(2)) ..				\$740.00	
Neither international preliminary examination fee (37 CFR §1.482) nor international search fee (37 CFR §1.445(a)(2)) paid to USPTO.....				\$1040 00	
International preliminary examination fee paid to USPTO (37 CFR §1.482) and all claims satisfied provisions of PCT Article 33(2)-(4). ....				\$100 00	
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				\$890.00	
Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than months from the earliest claimed priority date (37 C.F.R. §1.492(e)) <input type="checkbox"/> 20 <input type="checkbox"/> 30					
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	12 - 20 =	0	x \$ 18 00	\$0.00	
Independent claims	1 - 3 =	0	x \$ 84 00	\$0.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$ 280.00		
<b>TOTAL OF ABOVE CALCULATIONS =</b>				\$890.00	
Reduction of 1/2 for filing by small entity, if applicable. A Verified Small Entity Statement must also be					
<b>SUBTOTAL =</b>				\$890.00	
Processing fee of <b>\$130.00</b> for furnishing the English translation later than months from the earliest claimed priority date (37 C.F.R. §1.492(f)). <input type="checkbox"/> 20 <input type="checkbox"/> 30					
<b>TOTAL NATIONAL FEE =</b>				\$890.00	
Fee for recording the enclosed assignment (37 C.F.R. §1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 C.F.R. §§3.28, 3.31). \$40 00 per property.					
<b>TOTAL FEES ENCLOSED =</b>				\$890.00	
				Amount to be refunded	
				charged.	

- a. ☒ A check in the amount of \$890.00 to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No 13-3402 in the amount of \$\_\_\_\_\_ to cover the above fees. A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 13-3402. A duplicate copy of this sheet is enclosed.

**NOTE: Where an appropriate time limit under 37 C.F.R. §§1.494 or 1.495 has not been met, a petition to revive (37 C.F.R. §1.137(a) or (b)) must be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO: Customer Number 23,599

  
**23599**  
PATENT TRADEMARK OFFICE

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SIGNATURE  
Anthony J. Zelano  
NAME  

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27,969  
REGISTRATION NUMBER

Filed: 8 APRIL 2002  
AJZ:kmo

**IN THE UNITED STATES DESIGNATED/ELECTED OFFICE**

International Application No. : PCT/EP000/09133  
International Filing Date : 18 SEPTEMBER 2000  
Priority Date(s) Claimed : 6 OCTOBER 1999  
Applicant(s) (DO/EO/US) : REIFFENRATH, Volker, et al.

Title: LIQUID-CRYSTALLINE PHENOL ESTERS

**PRELIMINARY AMENDMENT**

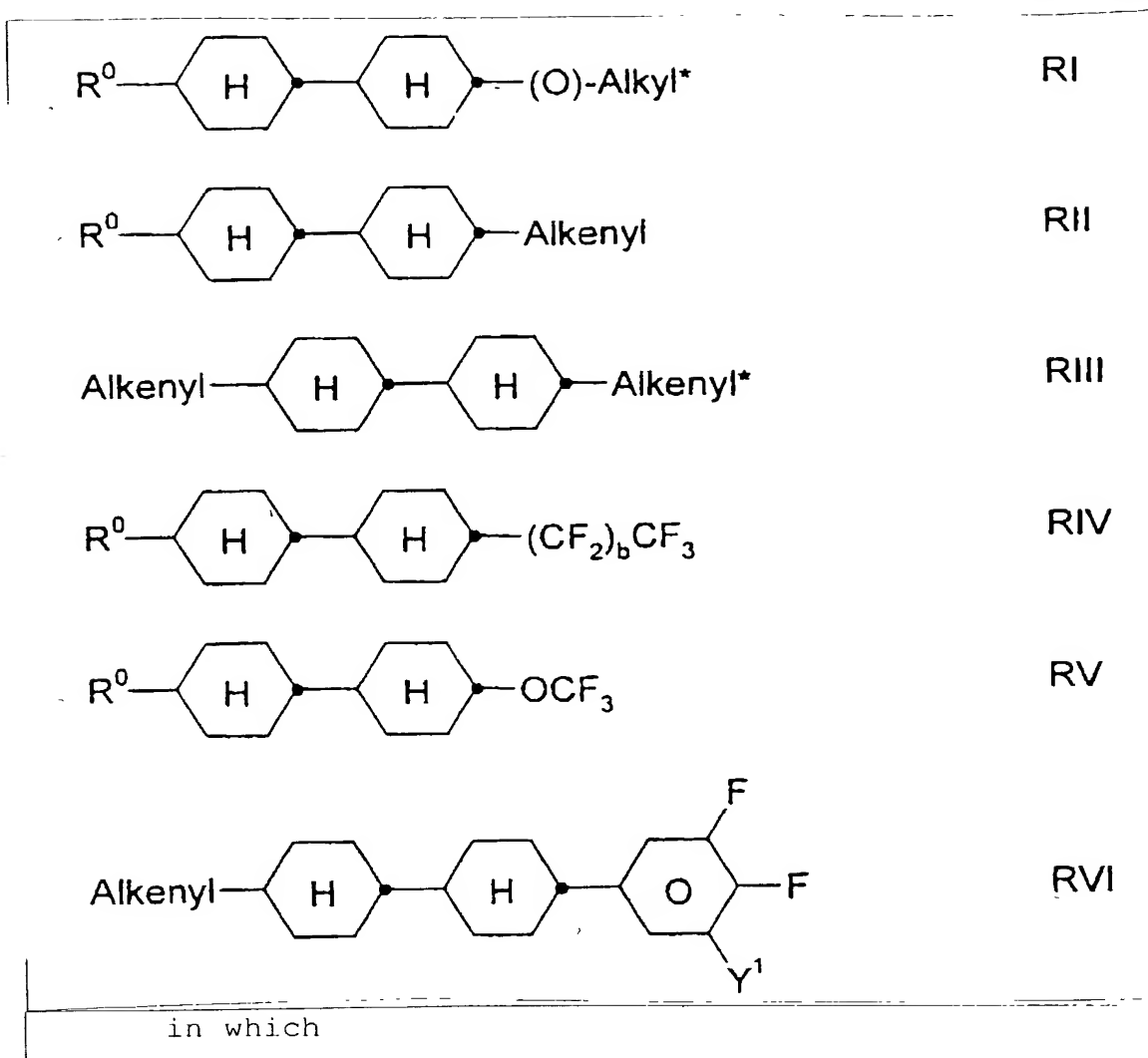
Commissioner for Patents  
Washington, D.C. 20231

SIR:

Prior to calculating the national fee, and prior to examination in the National Phase of the above-identified International application, please amend as follows:

**IN THE CLAIMS:**

4. (Amended) Phenol esters according to Claim 1, characterized in that  $M = 1$ .
8. (Amended) Medium according to Claim 6, characterized in that the proportion of compounds of the formulae I to IX in the total mixture is at least 50% by weight.
9. (Amended) Medium according to Claim 6, characterized in that it additionally comprises one or more compounds of the formulae RI to RVI



$R^0$  is n-alkyl, oxoalkyl, fluoroalkyl, alkenyloxy or alkenyl, in each case having up to 9 carbon atoms,

b is 0, 1 or 2,

$Y^1$  is H or F,

Alkyl\* is a straight-chain alkyl radical having up to 9 carbon atoms,

Alkenyl or Alkenyl\*

is, in each case independently of one another, an alkenyl radical having up to 9 carbon atoms.

10. (Amended) Medium according to Claim 7, characterized in that  $X^0$  is F or  $OCF_3$  and  $Y^2$  is H or F.

REMARKS

The purpose of this Preliminary Amendment is to eliminate multiple dependent claims in order to avoid the additional fee. Applicants reserve the right to reintroduce claims to canceled combined subject matter.

Attached hereto is a marked-up version of the changes made to the claims by the current amendment. The attached pages are captioned **“Version With Markings to Show Changes Made”**.

- Respectfully submitted,

  
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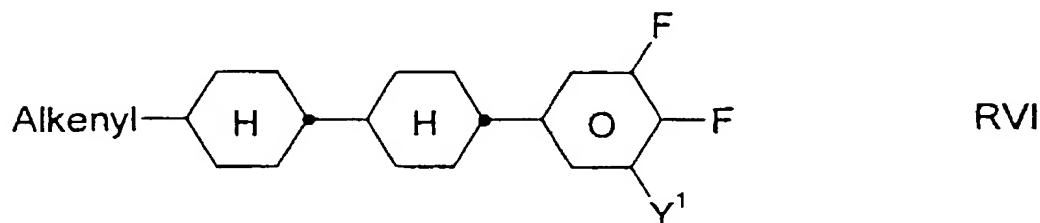
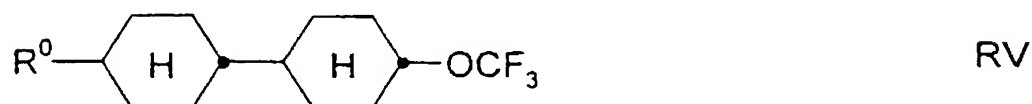
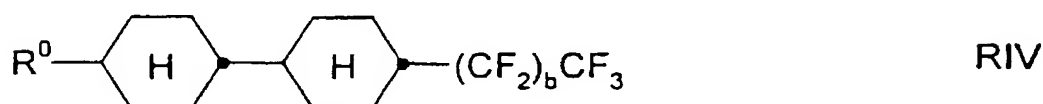
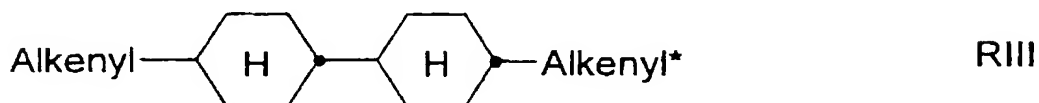
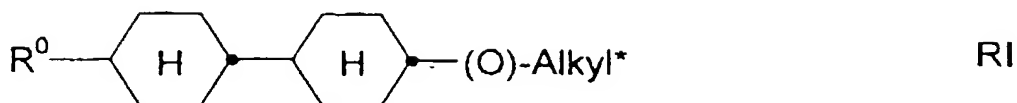
**VERSION WITH MARKINGS TO SHOW CHANGES MADE**

Claims 4 and 8-10 were amended:

4. (Amended) Phenol esters according to ~~one of~~ Claims 1 ~~to 3~~, characterized in that  $M = 1$ .

8. (Amended) Medium according to Claim 6 ~~or 7~~, characterized in that the proportion of compounds of the formulae I to IX in the total mixture is at least 50% by weight.

9. (Amended) Medium according to ~~one of~~ Claims 6 ~~to 8~~, characterized in that it additionally comprises one or more compounds of the formulae RI to RVI



in which

$R^0$  is n-alkyl, oxoalkyl, fluoroalkyl, alkenyloxy or alkenyl, in each case having up to 9 carbon atoms,

b is 0, 1 or 2,

$Y^1$  is H or F,

Alkyl\* is a straight-chain alkyl radical having up to 9 carbon atoms,

Alkenyl or Alkenyl\*

is, in each case independently of one another, an alkenyl radical having up to 9 carbon atoms.

10. (Amended) Medium according to one of Claims 7 to 9, characterized in that  $X^0$  is F or  $OCF_3$  and  $Y^2$  is H or F.



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Merck Patent Gesellschaft  
mit beschränkter Haftung  
64271 Darmstadt

Liquid-crystalline phenol esters

### Liquid-crystalline phenol esters

The present invention relates to liquid-crystalline phenol esters, to a liquid-crystalline medium, to the  
5 use thereof for electro-optical purposes and to displays containing this medium.

Liquid crystals are used, in particular, as dielectrics in display devices, since the optical properties of  
10 such substances can be modified by an applied voltage. Electro-optical devices based on liquid crystals are extremely well known to the person skilled in the art and can be based on various effects. Examples of such devices are cells having dynamic scattering, DAP  
15 (deformation of aligned phases) cells, guest/host cells, TN cells having a twisted nematic structure, STN (supertwisted nematic) cells, SBE (superbirefringence effect) cells and OMI (optical mode interference) cells. The most common display devices are based on the  
20 Schadt-Helfrich effect and have a twisted nematic structure.

The liquid-crystal materials must have good chemical and thermal stability and good stability to electric  
25 fields and electromagnetic radiation. Furthermore, the liquid-crystal materials should have low viscosity and give short response times, low threshold voltages and high contrast in the cells.

30 They should furthermore have a suitable mesophase, for example a nematic or cholesteric mesophase for the abovementioned cells, at conventional operating temperatures, i.e. in the broadest possible range above and below room temperature. Since liquid crystals are  
35 generally used as mixtures of a plurality of components, it is important that the components are readily miscible with one another. Further properties, such as the electrical conductivity, the dielectric anisotropy and the optical anisotropy, must satisfy

- 2 -

various requirements depending on the cell type and area of application. For example, materials for cells having a twisted nematic structure should have positive dielectric anisotropy and low electrical conductivity.

5

For example, media having large positive dielectric anisotropy, broad nematic phases, relatively low birefringence, very high resistivity, good UV and temperature stability and low vapour pressure are desired for matrix liquid-crystal displays containing integrated non-linear elements for switching individual pixels (MLC displays).

10

Matrix liquid-crystal displays of this type are known. Non-linear elements which can be used for individual switching of the individual pixels are, for example, active elements (i.e. transistors). This is then referred to as an "active matrix", and a distinction can be made between two types:

15

20

1. MOS (metal oxide semiconductor) or other diodes on a silicon wafer as substrate.
2. Thin-film transistors (TFTs) on a glass plate as substrate.

25

Use of single-crystal silicon as substrate material limits the display size, since even modular assembly of various part-displays results in problems at the joints.

30

In the case of the more promising type 2, which is preferred, the electro-optical effect used is usually the TN effect. A distinction is made between two technologies: TFTs comprising compound semiconductors, for example CdSe, or TFTs based on polycrystalline or amorphous silicon. Intensive work is being carried out worldwide on the latter technology.

35

- 3 -

The TFT matrix is applied to the inside of one glass plate of the display, while the other glass plate carries the transparent counterelectrode on its inside. Compared with the size of the pixel electrode, the TFT is very small and has virtually no adverse effect on the image. This technology can also be expanded to fully colour-compatible displays, in which a mosaic of red, green and blue filters is arranged in such a way that each filter element is located opposite a switchable pixel.

The TFT displays usually operate as TN cells with crossed polarizers in transmission and are backlit.

The term MLC displays here covers any matrix display containing integrated non-linear elements, i.e., besides the active matrix, also displays containing passive elements, such as varistors or diodes (MIM = metal-insulator-metal).

MLC displays of this type are particularly suitable for TV applications (for example pocket TVs) or for high-information displays for computer applications (laptops) and in automobile or aircraft construction. Besides problems regarding the angle dependence of the contrast and the response times, difficulties also arise in MLC displays due to inadequate resistivity of the liquid-crystal mixtures [TOGASHI, S., SEKIGUCHI, K., TANABE, H., YAMAMOTO, E., SORIMACHI, K., TAJIMA, E., WATANABE, H., SHIMIZU, H., Proc. Eurodisplay 84, Sept. 1984: A 210-288 Matrix LCD Controlled by Double Stage Diode Rings, p. 141 ff, Paris; STROMER, M., Proc. Eurodisplay 84, Sept. 1984: Design of Thin Film Transistors for Matrix Addressing of Television Liquid Crystal Displays, p. 145 ff, Paris]. With decreasing resistance, the contrast of an MLC display drops, and the problem of after-image elimination can occur. Since the resistivity of the liquid-crystal mixture generally drops over the life of

- 4 -

an MLC display owing to interaction with the interior surfaces of the display, a high (initial) resistance is very important in order to obtain acceptable service lives. In particular in the case of low-volt mixtures, it was hitherto impossible to achieve very high resistivity values. It is furthermore important that the resistivity increases as little as possible with increasing temperature and after heating and/or UV exposure. The low-temperature properties of the mixtures of the prior art are also particularly disadvantageous. It is required that crystallization and/or smectic phases do not occur, even at low temperatures, and that the temperature dependence of the viscosity is as low as possible. The MLC displays of the prior art thus do not satisfy today's requirements.

There thus continues to be a great demand for MLC displays which have very high resistivity at the same time as a broad operating temperature range, short response times, even at low temperatures, and a low threshold voltage, and which do not have these disadvantages, or only do so to a reduced extent.

In TN (Schadt-Helfrich) cells, media are desired which facilitate the following advantages in the cells:

- expanded nematic phase range (in particular down to low temperatures)
- switchability at extremely low temperatures (outdoor use, automobile, avionics)
- increased resistance to UV radiation (longer life)

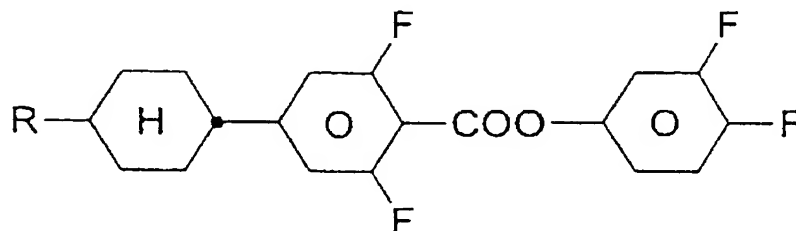
The media available from the prior art do not allow these advantages to be achieved while simultaneously retaining the other parameters.

- 5 -

In the case of supertwisted (STN) cells, media are desired which enable greater multiplexability and/or lower threshold voltages and/or broader nematic phase ranges (in particular at low temperatures). To this end, a further extension of the parameter latitude available (clearing point, smectic-nematic transition or melting point, viscosity, dielectric parameters, elastic parameters) is urgently desired.

It is an object of the invention to provide media, in particular for these MLC, TN or STN displays, which do not have the abovementioned disadvantages or only do so to a reduced extent, and preferably at the same time have very high resistivity values and low threshold voltages.

WO 92/05 230 discloses compounds of the formula

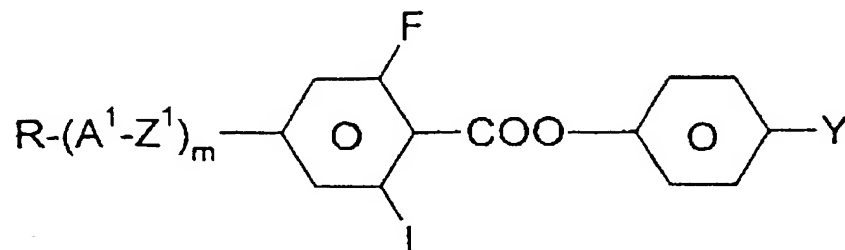


which, however, have comparatively low clearing points.

It has now been found that this object can be achieved by using the liquid-crystalline phenol esters according to the invention.

25

The invention thus relates to liquid-crystalline phenol esters of the formula I



I

in which

5 R is H, an alkyl or alkenyl radical having up to  
15 carbon atoms which is unsubstituted,  
monosubstituted by CN or CF<sub>3</sub> or at least  
monosubstituted by halogen, where one or more  
CH<sub>2</sub> groups in these radicals may also be  
10 replaced by -O-, -S-, -C≡C-, -OC-O- or -O-CO-  
in such a way that O atoms are not linked  
directly to one another,

15 A<sup>1</sup> a) is a 1,4-cyclohexenylene or 1,4-cyclo-  
hexylene radical, in which one or two non-  
adjacent CH<sub>2</sub> groups may be replaced by -O-  
or -S-,

20 b) is a 1,4-phenylene radical, in which one  
or two CH groups may be replaced by N,

25 c) is a piperidine-1,4-diyl, 1,4-bicyclo-  
[2.2.2]octylene, naphthalene-2,6-diyl,  
decahydronaphthalene-2,6-diyl or 1,2,3,4-  
tetrahydronaphthalene-2,6-diyl radical,

where the radicals a), b) and c) may be monosubstituted  
or polysubstituted by halogen atoms,

30 Z<sup>1</sup> is -CO-O-, -O-CO-, -CF<sub>2</sub>O-, -OCF<sub>2</sub>-, -CH<sub>2</sub>O-,  
-OCH<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>-, -C<sub>2</sub>F<sub>4</sub>-, -CH=CH-, -C≡C- or a  
single bond,

35 Y is F, Cl, CN or a monohalogenated or  
polyhalogenated alkyl, alkenyl, alkenyloxy or  
alkoxy radical having 1 to 5 carbon atoms,

L is H or F, and

m is 0, 1 or 2,

and to the use thereof in liquid-crystalline media.

5 The compounds of the formula I have a broad range of applications. Depending on the choice of substituents, these compounds can serve as base materials of which liquid-crystalline media are predominantly composed; however, it is also possible to add compounds of the formula I to liquid-crystalline base materials from  
10 other classes of compound in order, for example, to modify the dielectric and/or optical anisotropy of a dielectric of this type and/or to optimize its threshold voltage and/or its viscosity.

15 In the pure state, the compounds of the formula I are colourless and form liquid-crystalline mesophases in a temperature range which is favourably located for electro-optical use. The compounds according to the invention are particularly notable for their high  
20 clearing point. They are stable chemically, thermally and to light.

In particular, the invention relates to compounds of the formula I, in which R is alkyl having 1 to 10  
25 carbon atoms or an alkenyl radical having 2 to 10 carbon atoms.

Particular preference is given to compounds of the formula I in which L is F. m is preferably 1. Z<sup>1</sup> is  
30 preferably a single bond, furthermore -CF<sub>2</sub>O-, -OCF<sub>2</sub>-, -C<sub>2</sub>F<sub>4</sub>-, -CH<sub>2</sub>O-, -OCH<sub>2</sub>- or -COO-.

If R is an alkyl radical and/or an alkoxy radical, this can be straight-chain or branched. It is preferably  
35 straight-chain, has 2, 3, 4, 5, 6 or 7 carbon atoms and accordingly is preferably ethyl, propyl, butyl, pentyl, hexyl, heptyl, ethoxy, propoxy, butoxy, pentoxy, hexoxy or heptoxy, furthermore methyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl,



methoxy, octoxy, nonoxy, decoxy, undecoxy, dodecoxy, tridecoxy or tetradecoxy.

Oxaalkyl is preferably straight-chain 2-oxapropyl  
 5 (= methoxymethyl), 2- (= ethoxymethyl) or 3-oxabutyl  
 (= 2-methoxyethyl), 2-, 3- or 4-oxapentyl, 2-, 3-, 4-  
 or 5-oxahexyl, 2-, 3-, 4-, 5- or 6-oxaheptyl, 2-, 3-,  
 4-, 5-, 6- or 7-oxaoctyl, 2-, 3-, 4-, 5-, 6-, 7- or  
 8-oxanonyl, or 2-, 3-, 4-, 5-, 6-, 7-, 8- or  
 10 9-oxadecyl.

If R is an alkenyl radical, this can be straight-chain  
 or branched. It is preferably straight-chain and has 2  
 to 10 carbon atoms. Accordingly, it is in particular  
 15 vinyl, prop-1- or prop-2-enyl, but-1-, -2- or  
 but-3-enyl, pent-1-, -2-, -3- or pent-4-enyl, hex-1-,  
 -2-, -3-, -4- or hex-5-enyl, hept-1-, -2-, -3-, -4-,  
 -5- or hept-6-enyl, oct-1-, -2-, -3-, -4-, -5-, -6- or  
 oct-7-enyl, non-1-, -2-, -3-, -4-, -5-, -6-, -7- or  
 20 non-8-enyl, dec-1-, -2-, -3-, -4-, -5-, -6-, -7-, -8-  
 or dec-9-enyl.

If R is an alkyl radical in which one CH<sub>2</sub> group has been  
 replaced by -O- and one has been replaced by -CO-,  
 25 these are preferably adjacent. These thus contain an  
 acyloxy group -CO-O- or an oxycarbonyl group -O-CO-.  
 These are preferably straight-chain and have 2 to 6  
 carbon atoms.

30 They are accordingly in particular acetyloxy,  
 propionyloxy, butyryloxy, pentanoyloxy, hexanoyloxy,  
 acetyloxymethyl, propionyloxymethyl, butyryloxymethyl,  
 pentanoyloxymethyl, 2-acetyloxyethyl, 2-propionyloxy-  
 ethyl, 2-butyryloxyethyl, 3-acetyloxypropyl,  
 35 3-propionyloxypropyl, 4-acetyloxybutyl, methoxy-  
 carbonyl, ethoxycarbonyl, propoxycarbonyl, butoxy-  
 carbonyl, pentoxycarbonyl, methoxycarbonylmethyl,  
 ethoxycarbonylmethyl, propoxycarbonylmethyl, butoxy-  
 carbonylmethyl, 2-(methoxycarbonyl)ethyl, 2-(ethoxy-

carbonyl)ethyl, 2-(propoxycarbonyl)ethyl, 3-(methoxycarbonyl)propyl, 3-(ethoxycarbonyl)propyl or 4-(methoxycarbonyl)butyl.

- 5 If R is an alkyl or alkenyl radical which is monosubstituted by CN or CF<sub>3</sub>, this radical is preferably straight-chain. The substitution by CN or CF<sub>3</sub> is in any position.
- 10 If R is an alkyl or alkenyl radical which is at least monosubstituted by halogen, this radical is preferably straight-chain and halogen is preferably F or Cl. In the case of polysubstitution, halogen is preferably F. The resulting radicals also include perfluorinated
- 15 radicals. In the case of monosubstitution, the fluoro or chloro substituent can be in any desired position, but is preferably in the ω-position.

Compounds of the formula I containing branched pendant groups R may occasionally be of importance owing to better solubility in the conventional liquid-crystalline base materials, but in particular as chiral dopants if they are optically active. Smectic compounds of this type are suitable as components for ferro-

20 electric materials.

25

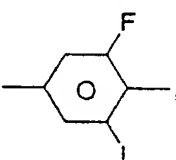
Compounds of the formula I having S<sub>A</sub> phases are suitable, for example, for thermally addressed displays.


- 30 Branched groups of this type generally contain not more than one chain branch. Preferred branched radicals R are isopropyl, 2-butyl (= 1-methylpropyl), isobutyl (= 2-methylpropyl), 2-methylbutyl, isopentyl
- 35 (= 3-methylbutyl), 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl, 2-propylpentyl, isopropoxy, 2-methylpropoxy, 2-methylbutoxy, 3-methylbutoxy, 2-methylpentoxy, 3-methylpentoxy, 2-ethylhexoxy, 1-methylhexoxy or 1-methylheptoxy.

Y is preferably F, Cl, CN, CF<sub>3</sub>, CF<sub>2</sub>H, OCF<sub>3</sub>, OCF<sub>2</sub>H, OCFHCF<sub>3</sub>, OCFHCFH<sub>2</sub>, OCFHCF<sub>2</sub>H, OCF<sub>2</sub>CH<sub>3</sub>, OCF<sub>2</sub>CFH<sub>2</sub>, OCF<sub>2</sub>CF<sub>2</sub>H, OCF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>H, OCF<sub>2</sub>CF<sub>2</sub>CFH<sub>2</sub>, OCFHCF<sub>2</sub>CF<sub>3</sub>, OCFHCF<sub>2</sub>CF<sub>2</sub>H, OCFHCFHCF<sub>3</sub>, OCH<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>, OCF<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>, OCF<sub>2</sub>CFHCFH<sub>2</sub>, OCF<sub>2</sub>CH<sub>2</sub>CF<sub>2</sub>H, OCFHCF<sub>2</sub>CFH<sub>2</sub>, OCFHCFHCF<sub>2</sub>H, OCFHCH<sub>2</sub>CF<sub>3</sub>, OCH<sub>2</sub>CFHCF<sub>3</sub>, OCH<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>H, OCF<sub>2</sub>CFHCH<sub>3</sub>, OCF<sub>2</sub>CH<sub>2</sub>CFH<sub>2</sub>, OCFHCF<sub>2</sub>CH<sub>3</sub>, OCFHCFHCFH<sub>2</sub>, OCFHCH<sub>2</sub>CF<sub>3</sub>, OCH<sub>2</sub>CF<sub>2</sub>CFH<sub>2</sub>, OCH<sub>2</sub>CFHCF<sub>2</sub>H, OCF<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, OCFHCFHCH<sub>3</sub>, OCFHCH<sub>2</sub>CFH<sub>2</sub>, OCH<sub>2</sub>CF<sub>2</sub>CH<sub>3</sub>, OCH<sub>2</sub>CFHCFH<sub>2</sub>, OCH<sub>2</sub>CH<sub>2</sub>CF<sub>2</sub>H, OCHCH<sub>2</sub>CH<sub>3</sub>, OCH<sub>2</sub>CFHCH<sub>3</sub>, OCH<sub>2</sub>CH<sub>2</sub>CF<sub>2</sub>H, OCCIFCF<sub>3</sub>, OCCIFCCIF<sub>2</sub>, OCCIFCFH<sub>2</sub>, OCFHCCl<sub>2</sub>F, OCCIFCF<sub>2</sub>H, OCCIFCCIF<sub>2</sub>, OCF<sub>2</sub>CClH<sub>2</sub>, OCF<sub>2</sub>CCl<sub>2</sub>H, OCF<sub>2</sub>CCl<sub>2</sub>F, OCF<sub>2</sub>CCIFH, OCF<sub>2</sub>CCIF<sub>2</sub>, OCF<sub>2</sub>CF<sub>2</sub>CCIF<sub>2</sub>, OCF<sub>2</sub>CF<sub>2</sub>CCl<sub>2</sub>F,

OCCIFCF<sub>2</sub>CF<sub>3</sub>, OCCIFCF<sub>2</sub>CF<sub>2</sub>H, OCCIFCF<sub>2</sub>CCIF<sub>2</sub>, OCCIFCFHCF<sub>3</sub>, OCCIFCCIFCF<sub>3</sub>, OCCl<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>, OCClHCF<sub>2</sub>CF<sub>3</sub>, OCCIFCF<sub>2</sub>CF<sub>3</sub>, OCCIFCCIFCF<sub>3</sub>, OCF<sub>2</sub>CCIFCFH<sub>2</sub>, OCF<sub>2</sub>CF<sub>2</sub>CCl<sub>2</sub>F, OCF<sub>2</sub>CCl<sub>2</sub>CF<sub>2</sub>H, OCF<sub>2</sub>CH<sub>2</sub>CCIF<sub>2</sub>, OCCIFCF<sub>2</sub>CFH<sub>2</sub>, OCFHCF<sub>2</sub>CCl<sub>2</sub>F, OCCIFCFHCF<sub>2</sub>H, OCCIFCCIFCF<sub>2</sub>H, OCFHCFHCCIF<sub>2</sub>, OCCIFCH<sub>2</sub>CF<sub>3</sub>, OCFHCCl<sub>2</sub>CF<sub>3</sub>, OCCl<sub>2</sub>CFHCF<sub>3</sub>, OCH<sub>2</sub>CCIFCF<sub>3</sub>, OCCl<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>H, OCH<sub>2</sub>CF<sub>2</sub>CCIF<sub>2</sub>, OCF<sub>2</sub>CCIFCH<sub>3</sub>, OCF<sub>2</sub>CFHCCl<sub>2</sub>H, OCF<sub>2</sub>CCl<sub>2</sub>CFH<sub>2</sub>, OCF<sub>2</sub>CH<sub>2</sub>CCl<sub>2</sub>F, OCCIFCF<sub>2</sub>CH<sub>3</sub>, OCFHCF<sub>2</sub>CCl<sub>2</sub>H, OCCIFCCIFCFH<sub>2</sub>, OCFHCFHCCl<sub>2</sub>F, OCCIFCH<sub>2</sub>CF<sub>3</sub>, OCFHCCl<sub>2</sub>CF<sub>3</sub>, OCCl<sub>2</sub>CF<sub>2</sub>CFH<sub>2</sub>, OCH<sub>2</sub>CF<sub>2</sub>CCl<sub>2</sub>F, OCCl<sub>2</sub>CFHCF<sub>2</sub>H, OCClHCCIFCF<sub>2</sub>H, OCF<sub>2</sub>CClHCClH<sub>2</sub>, OCF<sub>2</sub>CH<sub>2</sub>CCl<sub>2</sub>H, OCCIFCFHCH<sub>3</sub>, OCF<sub>2</sub>CCIFCCl<sub>2</sub>H, OCCIFCH<sub>2</sub>CFH<sub>2</sub>, OCFHCCl<sub>2</sub>CFH<sub>2</sub>, OCCl<sub>2</sub>CF<sub>2</sub>CH<sub>3</sub>, OCH<sub>2</sub>CF<sub>2</sub>CClH<sub>2</sub>, OCCl<sub>2</sub>CFHCFH<sub>2</sub>, OCH<sub>2</sub>CCIFCFCl<sub>2</sub>, OCH<sub>2</sub>CH<sub>2</sub>CF<sub>2</sub>H, OCClHCClHCF<sub>2</sub>H, OCH<sub>2</sub>CCl<sub>2</sub>CF<sub>2</sub>H, OCCIFCH<sub>2</sub>CH<sub>3</sub>, OCFHCH<sub>2</sub>CCl<sub>2</sub>H, OCClHCFHCClH<sub>2</sub>, OCH<sub>2</sub>CFHCCl<sub>2</sub>H, OCCl<sub>2</sub>CH<sub>2</sub>CF<sub>2</sub>H, OCH<sub>2</sub>CCl<sub>2</sub>CF<sub>2</sub>H, CH=CF<sub>2</sub>, CF=CF<sub>2</sub>, OCH=CF<sub>2</sub>, OCF=CF<sub>2</sub>, CH=CHF, OCH=CHF, CF=CHF, OCF=CHF, in particular F, Cl, CN, CF<sub>3</sub>, CF<sub>2</sub>H, OCF<sub>3</sub>, OCF<sub>2</sub>H, OCFHCF<sub>3</sub>, OCFHCFH<sub>2</sub>, OCFHCF<sub>2</sub>H, OCF<sub>2</sub>CH<sub>3</sub>, OCF<sub>2</sub>CFH<sub>2</sub>, OCF<sub>2</sub>CF<sub>2</sub>H, OCF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>H, OCF<sub>2</sub>CF<sub>2</sub>CFH<sub>2</sub>, OCFHCF<sub>2</sub>CF<sub>3</sub>, OCFHCF<sub>2</sub>CF<sub>2</sub>H, OCF<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>, OCF<sub>2</sub>CHFCF<sub>3</sub>, OCCIFCF<sub>2</sub>CF<sub>3</sub>.

For reasons of simplicity, hereinafter A<sup>2</sup> is a radical

5 of the formula , Cyc is a 1,4-cyclohexylene

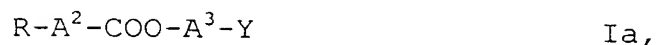
radical, A<sup>3</sup> is , Che is a 1,4-cyclohexenyl

radical, Dio is a 1,3-dioxane-2,5-diyl radical, Dit is

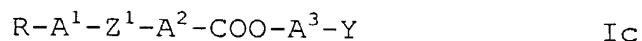
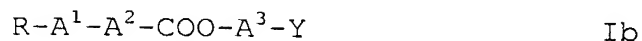
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a 1,3-dithiane-2,5-diyl radical, Phe is a 1,4-phenylene radical, Pyd is a pyridine-2,5-diyl radical, Pyr is a pyrimidine-2,5-diyl radical, Bi is a bicyclo[2.2.2]octylene radical, PheF is a 2- or 3-fluoro-1,4-phenylene radical, PheFF is a 2,6-difluoro-1,4-phenylene radical, Nap is a substituted or unsubstituted naphthalene radical and Dec is a decahydronaphthalene radical.

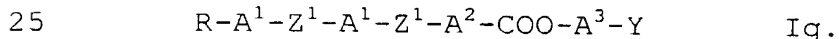
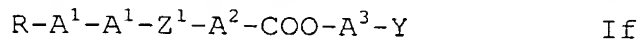
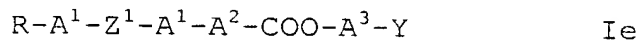
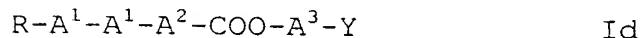
10 Accordingly, the compounds of the formula I include the preferred bicyclic compounds of the subformula Ia:



15 tricyclic compounds of the subformulae Ib and Ic:



20 and tetracyclic compounds of the subformulae Id to Ig:



In the subformulae Id to Ig, the rings  $A^1$  and the bridges  $Z^1$  can each be identical or different.

30 Of these, the compounds of the subformulae Ia, Ib and Ic are particularly preferred.

In the compounds of the formulae above and below, Y is preferably F, CN,  $OCF_3$ ,  $OCHF_2$ ,  $CF_3$ ,  $OCHF_2CF_3$ ,  $OC_2F_5$  or  
35  $OCF_2CH_2CF_3$ .

R is preferably straight-chain alkyl, alkoxy, alkenyloxy or alkenyl having up to 10 carbon atoms.

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A<sup>1</sup> is preferably Phe, PheF, PheFF, Cyc or Che, furthermore Pyr or Dio, Dec or Nap. The compounds of the formula I preferably contain not more than one of the radicals Bi, Pyd, Pyr, Dio, Dit, Nap or Dec.

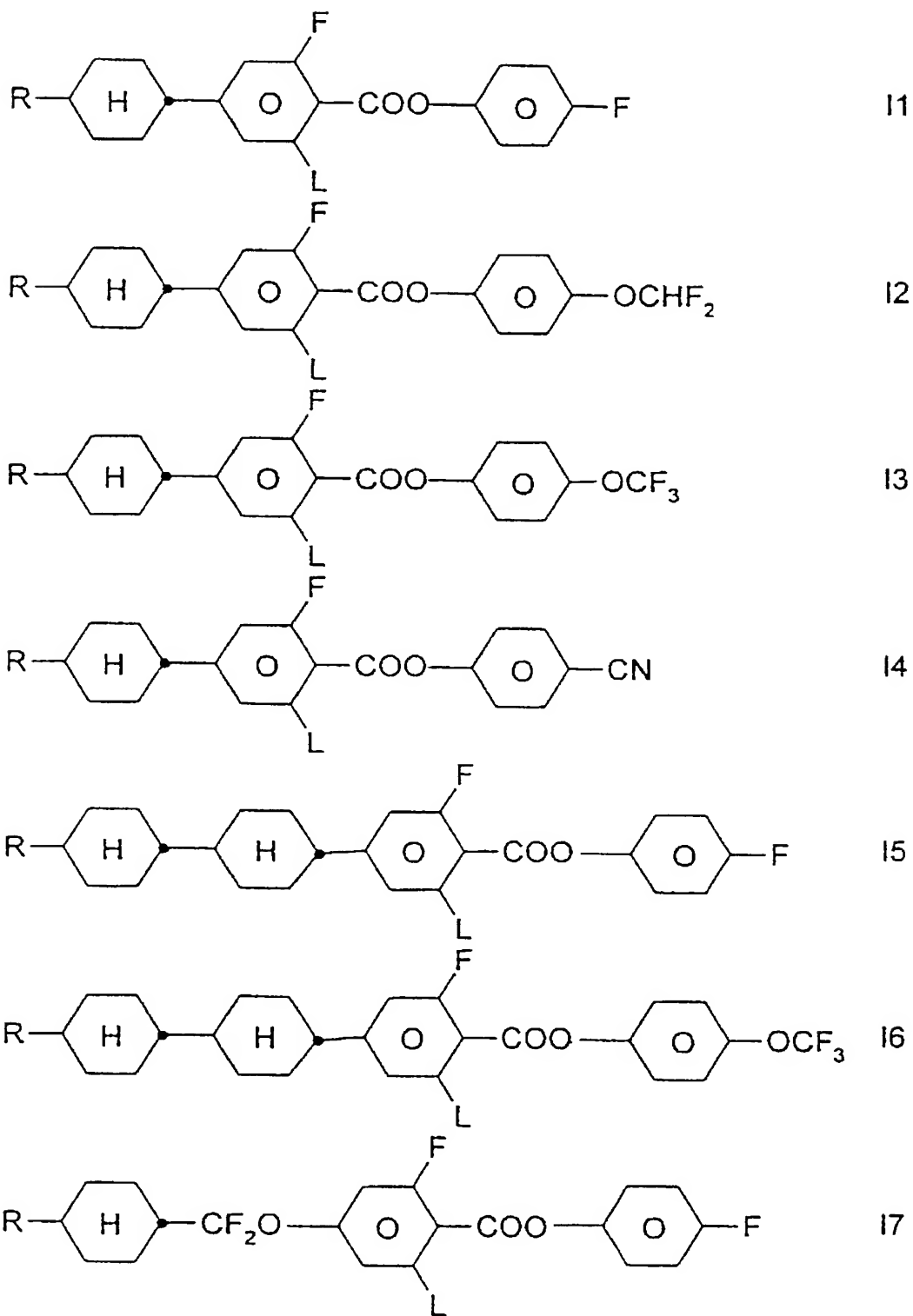
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Preference is also given to all compounds of the formula I and all subformulae, in which A<sup>1</sup> is monosubstituted or disubstituted 1,4-phenylene, in particular 2-fluoro-1,4-phenylene, 3-fluoro-1,4-phenylene, 2,3-difluoro-1,4-phenylene and 2,6-difluoro-1,4-phenylene.

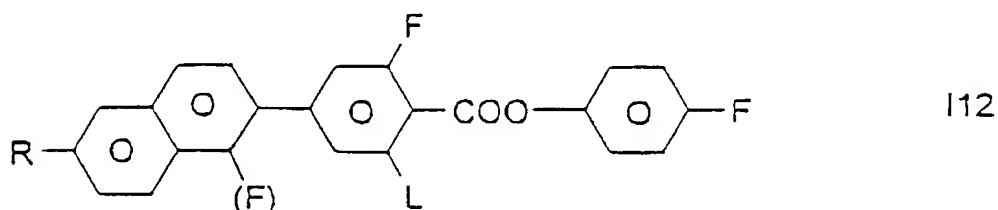
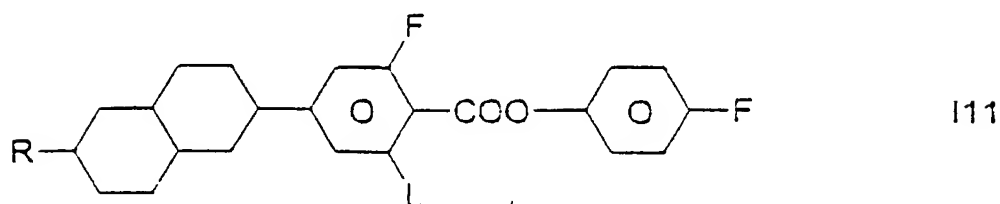
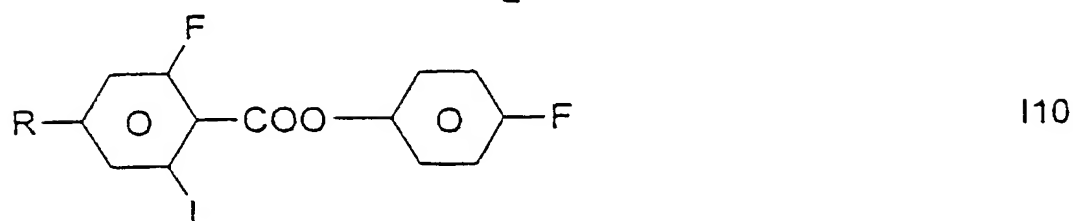
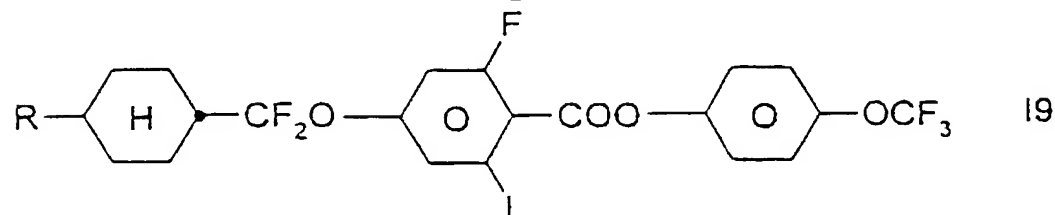
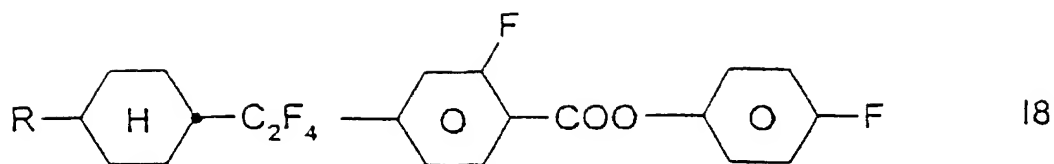
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Preferred smaller groups of compounds of the formula I are those of the subformulae I1 to I12:

15



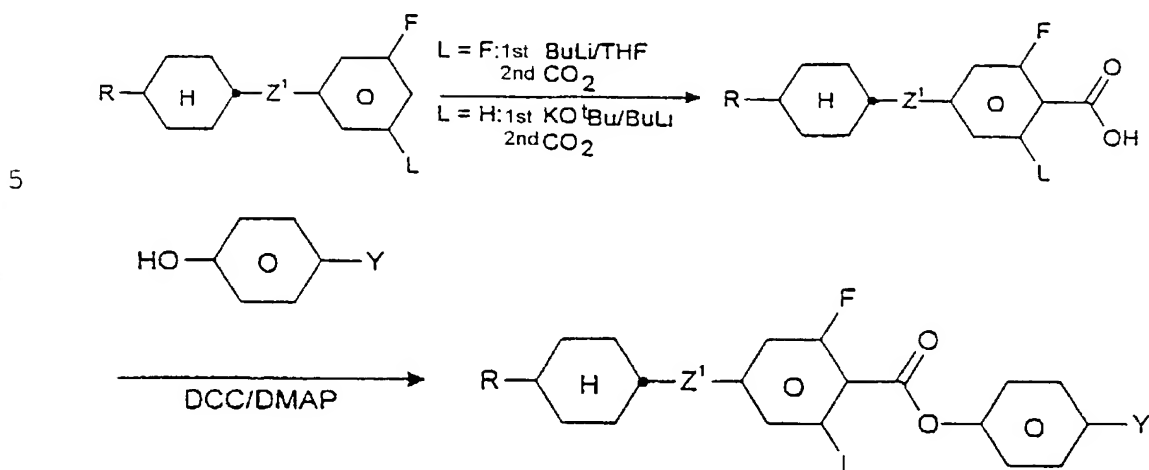
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The compounds of the formula I are prepared by methods  
 5 known per se, as described in the literature (for  
 example in the standard works, such as Houben-Weyl,  
 Methoden der Organischen Chemie, Georg-Thieme-Verlag,  
 Stuttgart), to be precise under reaction conditions  
 which are known and suitable for said reactions. Use  
 10 can also be made here of variants which are known per  
 se, but are not mentioned here in greater detail.

The esters of the formula I can be synthesized, for  
 example, from the corresponding acids and phenols with  
 15 elimination of water, for example by dicyclohexylcarbo-  
 diimide.

The compounds according to the invention can, for example, be prepared in accordance with the following scheme:



The invention also relates to electro-optical displays (in particular STN or MLC displays having two plane-parallel outer plates, which, together with a frame, form a cell, integrated non-linear elements for switching individual pixels on the outer plates, and a nematic liquid-crystal mixture of positive dielectric anisotropy and high resistivity which is located in the cell) which contain media of this type, and to the use of these media for electro-optical purposes.

The liquid-crystal mixtures according to the invention allow a significant extension of the parameter latitude which is available.

The achievable combinations of clearing point, viscosity at low temperature, thermal and UV stability and dielectric anisotropy are far superior to current prior-art materials.

The requirement for a high clearing point, nematic phase at low temperature and a high  $\Delta\epsilon$  has hitherto only been met inadequately. Although liquid-crystal mixtures such as, for example, MLC-6476 and MLC-6625 (Merck KGaA, Darmstadt, Germany) have comparable clear-



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ing points and low-temperature stabilities, they have, however, much higher  $\Delta n$  values of about 0.075 and much higher threshold voltages of about  $\geq 1.7$  V.

- 5 Other mixture systems have comparable viscosities and  $\Delta\epsilon$  values, but only have clearing points in the region of  $60^\circ\text{C}$ .

10 While maintaining the nematic phase down to  $-20^\circ\text{C}$ , preferably down to  $-30^\circ\text{C}$ , particularly preferably down to  $-40^\circ\text{C}$ , the liquid-crystal mixtures according to the invention allow clearing points above  $80^\circ\text{C}$ , preferably above  $90^\circ\text{C}$ , particularly preferably above  $100^\circ\text{C}$ , simultaneously dielectric anisotropy values  $\Delta\epsilon \geq 4$ ,  
15 preferably  $\geq 6$  and a high resistivity, allowing excellent STN and MLC displays to be achieved. In particular, the mixtures are characterized by low operating voltages. The TN thresholds are below 1.5 V, preferably below 1.3 V, particularly preferably  
20  $< 1.0$  V.

It goes without saying that a suitable choice of the components of the mixtures according to the invention also allows higher clearing points (for example above  
25  $110^\circ\text{C}$ ) to be achieved at higher threshold voltages, or lower clearing points to be achieved at lower threshold voltages, while retaining the other advantageous properties. Likewise, mixtures of higher  $\Delta\epsilon$  and thus lower thresholds can also be obtained at viscosities  
30 which are increased correspondingly little. The MLC displays according to the invention preferably operate at the first Gooch and Tarry transmission minimum [C.H. Gooch and H.A. Tarry, Electron. Lett. 10, 2-4, 1974; C.H. Gooch and H.A. Tarry, Appl. Phys., Vol. 8,  
35 1575-1584, 1975], where, besides particularly favourable electro-optical properties, such as, for example, high steepness of the characteristic line and low angle dependence of the contrast (German Patent 30 22 818), a lower dielectric anisotropy is sufficient

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at the same threshold voltage as in an analogous display at the second minimum. Thus, significantly higher resistivities can be achieved using the mixtures according to the invention at the first minimum than in  
 5 the case of mixtures comprising cyano compounds. A person skilled in the art can use simple routine methods to produce the birefringence necessary for a specified layer thickness of the MLC display by suitable choice of the individual components and their  
 10 proportions by weight.

The flow viscosity  $\eta_{20}$  at 20°C is preferably  $< 60 \text{ mm}^2 \cdot \text{s}^{-1}$ , particularly preferably  $< 50 \text{ mm}^2 \cdot \text{s}^{-1}$ . The nematic phase range is preferably at least 90°, in  
 15 particular at least 100°. This range preferably extends at least from -30° to +80°.

Measurements of the capacity holding ratio (HR) [S. Matsumoto et al., Liquid Crystals 5, 1320 (1989);  
 20 K. Niwa et al., Proc. SID Conference, San Francisco, June 1984, p. 304 (1984); G. Weber et al., Liquid Crystals 5, 1381 (1989)] show that mixtures according to the invention and comprising compounds of the formula I exhibit a considerably smaller drop in the HR  
 25 with increasing temperature than do analogous mixtures in which the compounds of the formula I are replaced by cyanophenylcyclohexanes of the formula  $\text{R}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$

or esters of the formula  $\text{R}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{C}_6\text{H}_3(\text{F})-\text{CN}$ .

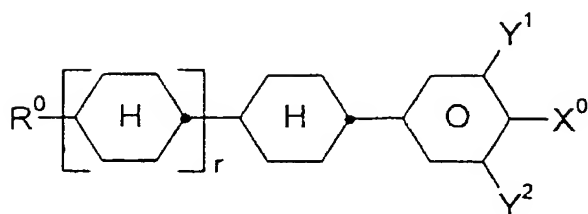
30 The UV stability of the mixtures according to the invention is also considerably better, i.e. they exhibit a significantly smaller drop in HR on UV exposure.

35 The media according to the invention are preferably based on a plurality (preferably two, three or more) of

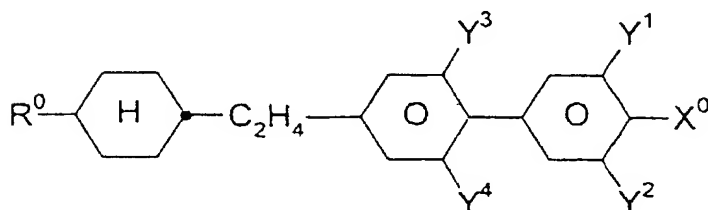
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compounds of the formula I, i.e. the proportion of these compounds is 5-95%, preferably 10-60%, and particularly preferably in the range 20-50%.

- 5 The individual compounds of the formulae I to IX and their subformulae which can be used in the media according to the invention are either known or can be prepared analogously to the known compounds.
- 10 Preferred embodiments are indicated below:
- The medium comprises compounds of the formula I, in which R is preferably ethyl and/or propyl, furthermore butyl and pentyl. Compounds of the formula I having short side chains R have a positive effect on the elastic constants, in particular  $K_1$ , and give mixtures having particularly low threshold voltages.
- 15
- The medium additionally comprises one or more compounds selected from the group consisting of the general formulae II to IX:
- 20

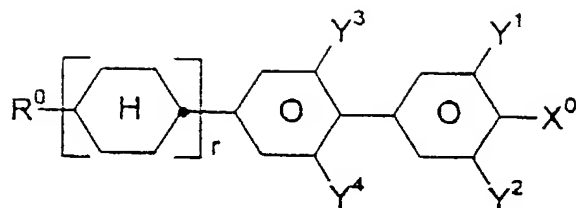


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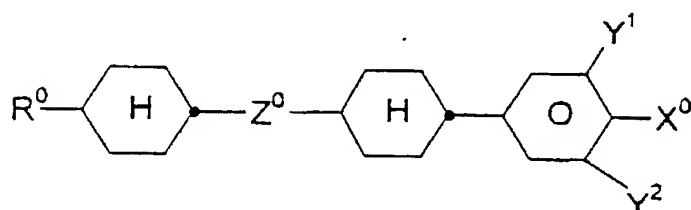


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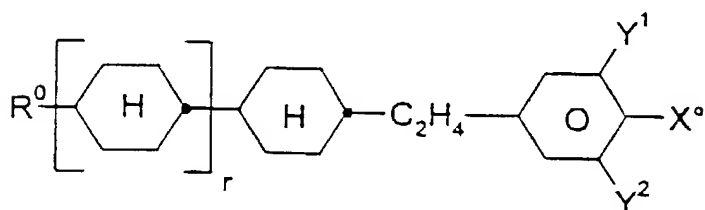
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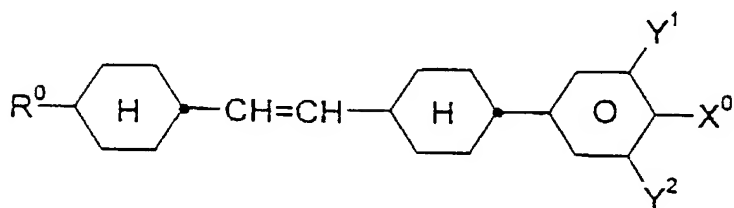
IV



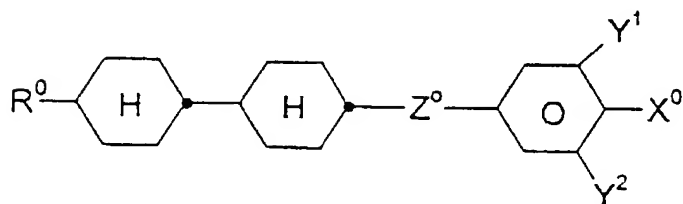
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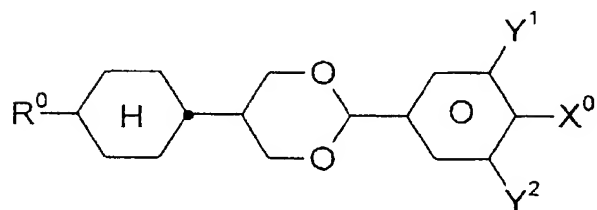
VI



VII



VIII



IX

in which the individual radicals have the following meanings:

- 10  $R^0$  is n-alkyl, oxaalkyl, fluoroalkyl, alkenyloxy or alkenyl, in each case having up to 9 carbon atoms,

- 20 -

$X^0$  is F, Cl, halogenated alkyl, alkenyl, alkenyloxy or alkoxy having 1 to 6 carbon atoms,

$Z^0$  is  $-C_2H_4-$ ,  $-C_2F_4-$ ,  $-CF_2O-$ ,  $-OCF_2-$  or  $-COO-$ ,

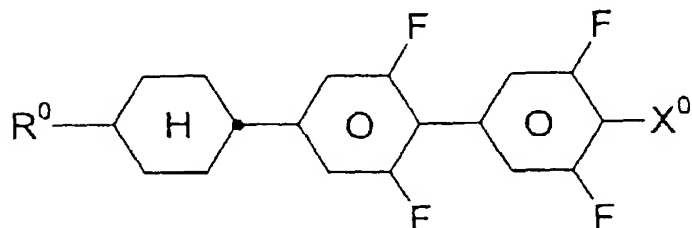
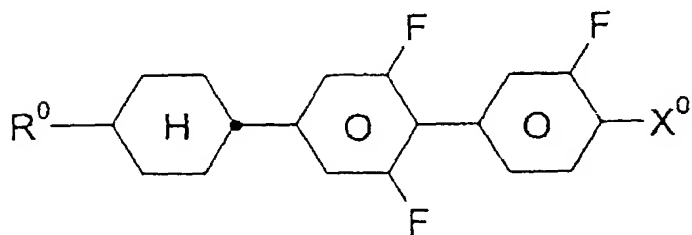
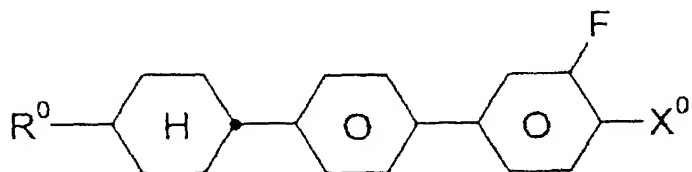
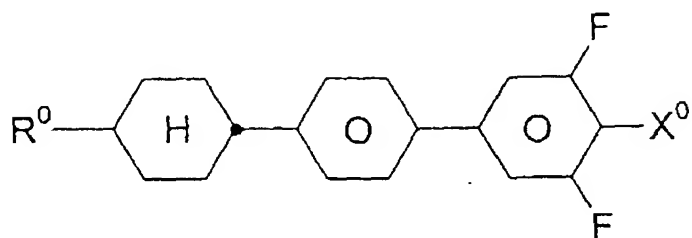
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$Y^1$ ,  $Y^2$ ,

$Y^3$  and  $Y^4$  are each, independently of one another, H or F, and

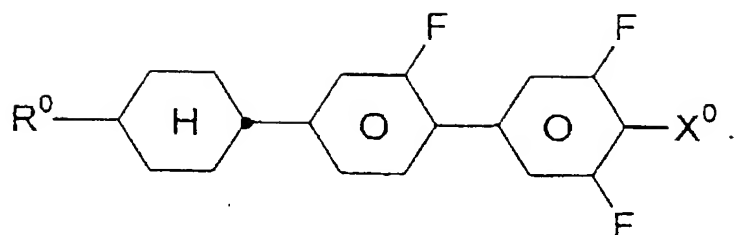
10  $r$  is 0 or 1.

The compound of the formula IV is preferably



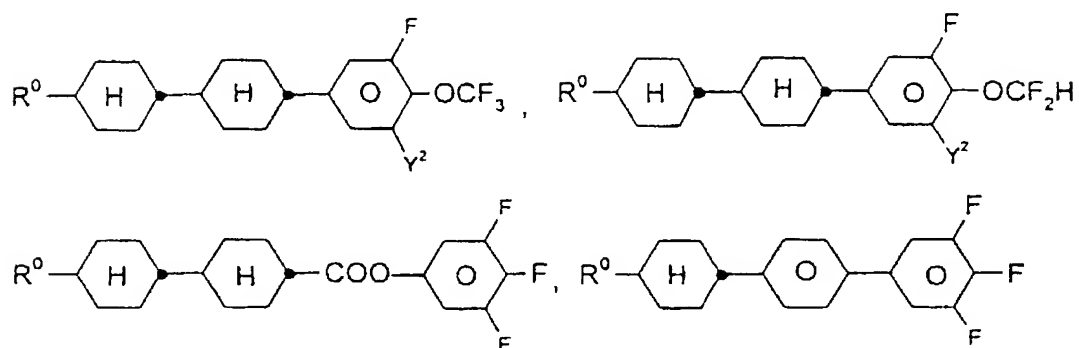
or

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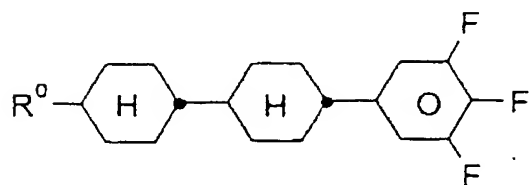


- The medium additionally comprises one or more compounds of the formulae

5



and/or



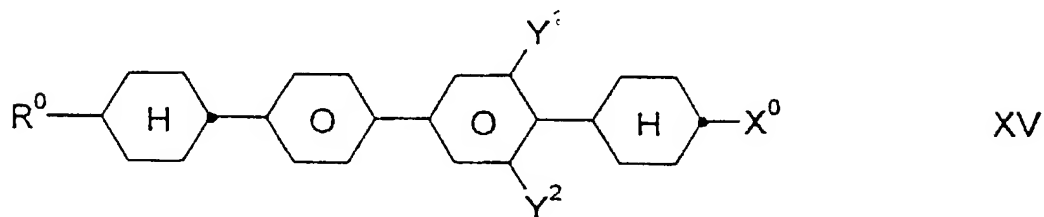
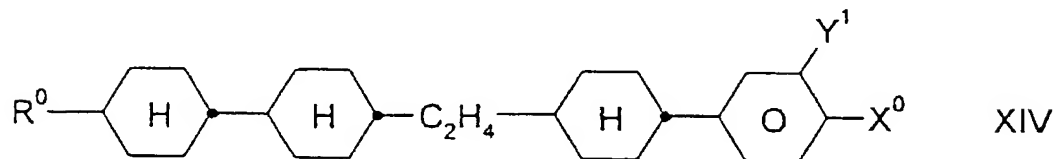
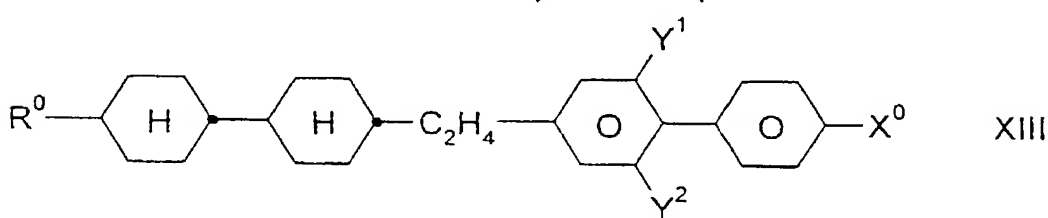
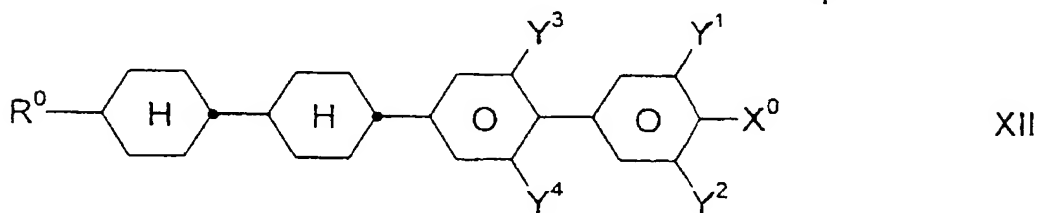
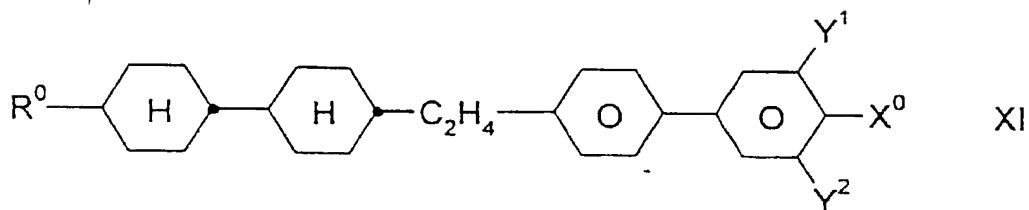
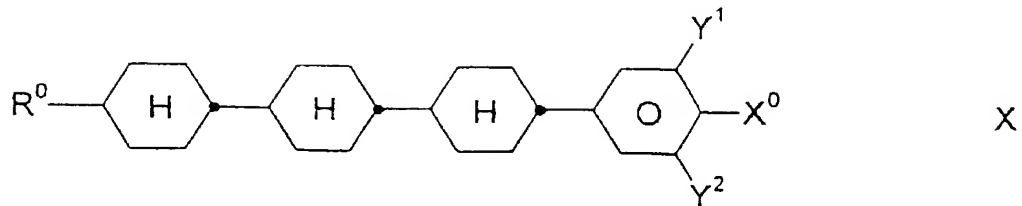
10

in which  $R^0$  and  $Y^2$  are as defined above.

- The medium additionally comprises one or more compounds selected from the group consisting of the general formulae X to XV:

15

- 22 -



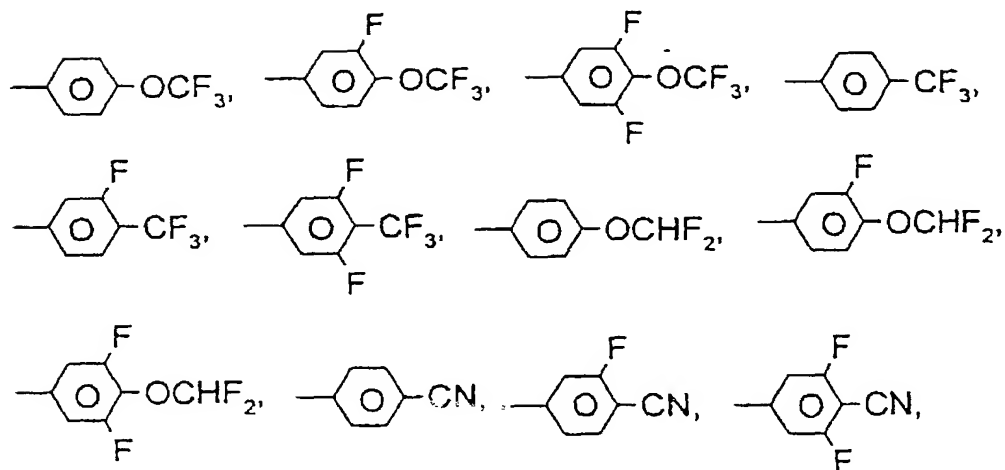
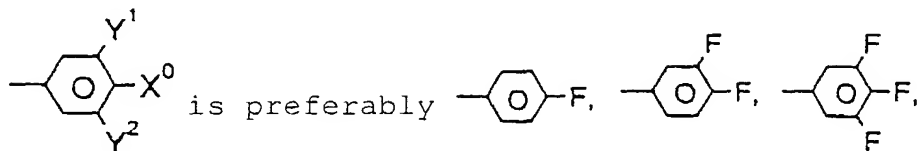
5 in which  $R^0$ ,  $X^0$ ,  $Y^1$ ,  $Y^2$ ,  $Y^3$  and  $Y^4$  are each, independently of one another, as defined in Claim 7.  $X^0$  is preferably F, Cl,  $CF_3$ ,  $OCF_3$ ,  $OCHF_2$ , and  $R^0$  is alkyl, oxaalkyl, fluoroalkyl, alkenyl or alkenyloxy, in each case having up to 6 carbon atoms.

- 23 -

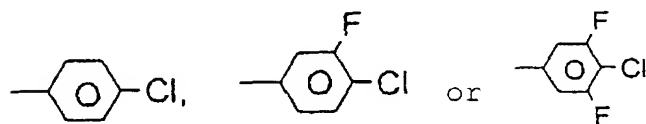
- The proportion of compounds of the formulae I to IX together in the total mixture is at least 50% by weight.

5 - The proportion of compounds of the formula I in the total mixture is from 5 to 50% by weight.

10 - The proportion of compounds of the formulae II to XI in the total mixture is from 30 to 70% by weight.



15



- The medium comprises compounds of the formulae II, III, IV, V, VI, VII, VIII and/or IX.

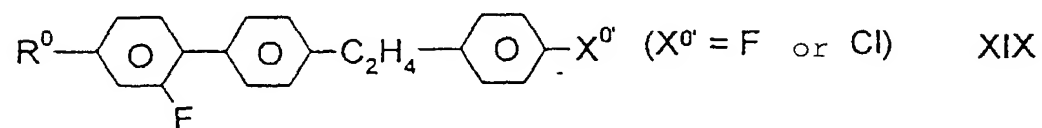
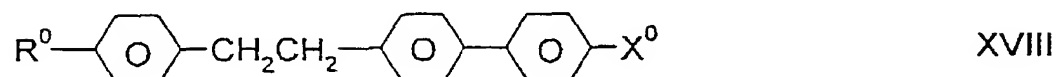
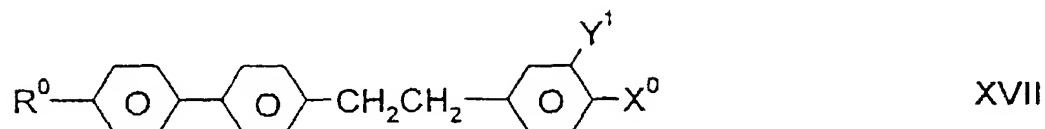
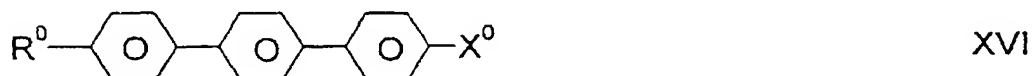
20

- R<sup>0</sup> is straight-chain alkyl or alkenyl having 2 to 6 carbon atoms.



- 24 -

- The medium essentially consists of compounds of the formulae I to XV.
- 5 - The medium comprises further compounds, preferably selected from the following group consisting of the general formulae XVI to XIX:



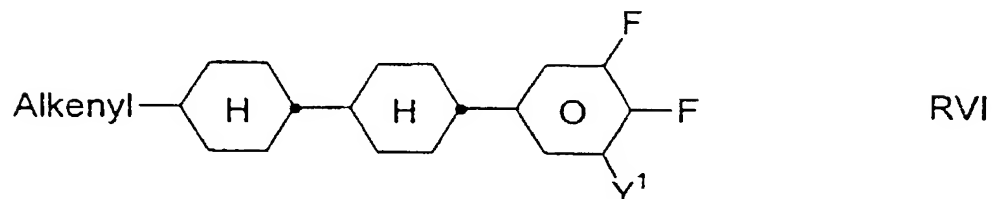
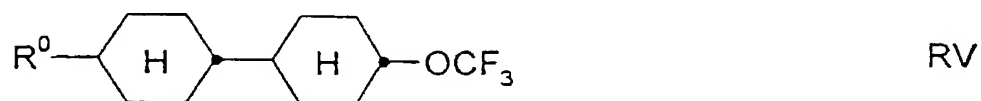
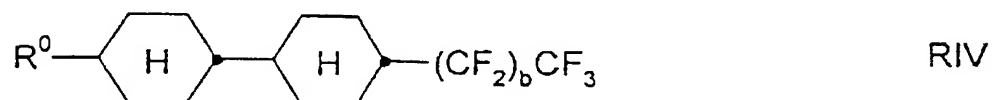
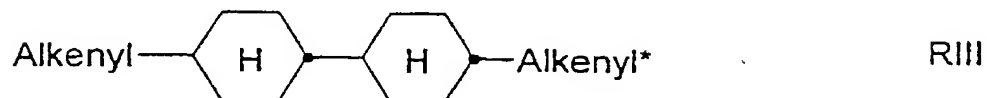
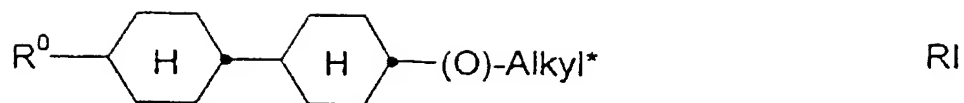
10

in which  $R^0$  and  $X^0$  are as defined above and the 1,4-phenylene rings can be substituted by CN, chlorine or fluorine. The 1,4-phenylene rings are preferably monosubstituted or polysubstituted by fluorine atoms.

15

- The medium comprises further compounds, preferably selected from the following group consisting of the formulae RI to RVI:

- 25 -



in which

5  $R^0$  is n-alkyl, oxoalkyl, fluoroalkyl, alkenyloxy or alkenyl, in each case having up to 9 carbon atoms,

b is 0, 1 or 2,

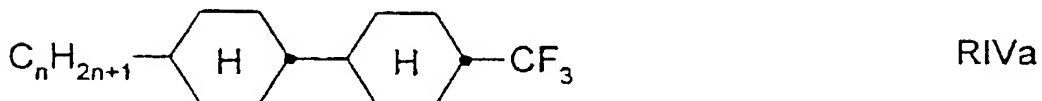
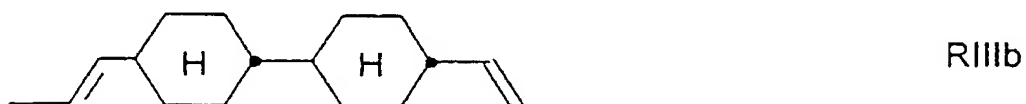
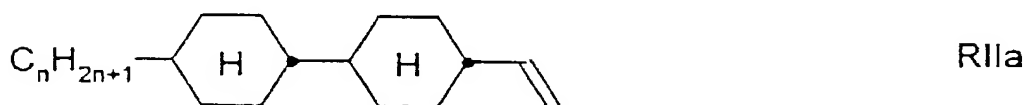
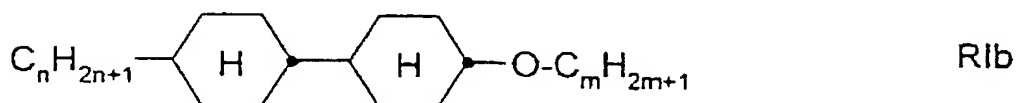
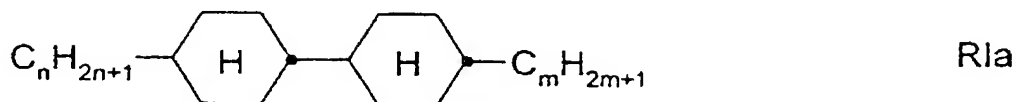
10  $Y^1$  is H or F,

Alkyl\* is a straight-chain alkyl radical having up to 9 carbon atoms,

15 Alkenyl or Alkenyl\* is, in each case independently of one another, an alkenyl radical having up to 9 carbon atoms.

- 26 -

- The medium preferably comprises one or more compounds of the formulae



5 in which n and m are each an integer from 1-9.

- The weight ratio I: (II + III + IV + V + VI + VII + VIII + IX) is preferably from 1:10 to 10:1.

10 - The medium essentially consists of compounds selected from the group consisting of the general formulae I to XV.

- 27 -

It has been found that even a relatively small proportion of compounds of the formula I mixed with conventional liquid-crystal materials, but in particular with one or more compounds of the formulae II, III, IV, V, VI, VII, VIII and/or IX leads to a considerable decrease in the threshold voltage and to low birefringence values, where broad nematic phases with low smectic-nematic transition temperatures are simultaneously observed, which improve the storage stability. The compounds of the formulae I to IX are colourless, stable and readily miscible with one another and with other liquid-crystal materials.

The term "alkyl" or "alkyl\*" encompasses straight-chain and branched alkyl groups having 1-9 carbon atoms, particularly the straight-chain groups methyl, ethyl, propyl, butyl, pentyl, hexyl and heptyl. Groups having 2-5 carbon atoms are generally preferred.

The term "alkenyl" or "alkenyl\*" encompasses straight-chain and branched alkenyl groups having up to 9 carbon atoms, in particular the straight-chain groups. Particularly preferred alkenyl groups are C<sub>2</sub>-C<sub>7</sub>-1E-alkenyl, C<sub>4</sub>-C<sub>7</sub>-3E-alkenyl, C<sub>5</sub>-C<sub>7</sub>-4-alkenyl, C<sub>6</sub>-C<sub>7</sub>-5-alkenyl and C<sub>7</sub>-6-alkenyl, in particular C<sub>2</sub>-C<sub>7</sub>-1E-alkenyl, C<sub>4</sub>-C<sub>7</sub>-3E-alkenyl and C<sub>5</sub>-C<sub>7</sub>-4-alkenyl. Examples of preferred alkenyl groups are vinyl, 1E-propenyl, 1E-butenyl, 1E-pentenyl, 1E-hexenyl, 1E-heptenyl, 3-butenyl, 3E-pentenyl, 3E-hexenyl, 3E-heptenyl, 4-pentenyl, 4Z-hexenyl, 4E-hexenyl, 4Z-heptenyl, 5-hexenyl, 6-heptenyl and the like. Groups having up to 5 carbon atoms are generally preferred.

The term "fluoroalkyl" preferably encompasses straight-chain groups with terminal fluorine, i.e. fluoromethyl, 2-fluoroethyl, 3-fluoropropyl, 4-fluorobutyl, 5-fluoropentyl, 6-fluorohexyl and 7-fluoroheptyl. Other positions of fluorine are not precluded, however.

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The term "oxaalkyl" preferably encompasses straight-chain radicals of the formula  $C_nH_{2n+1}-O-(CH_2)_m$ , in which  $n$  and  $m$  are each, independently of one another, from 1 to 6. Preferably,  $n = 1$  and  $m$  is 1 to 6.

5

A suitable choice of the meanings of  $R^0$  and  $X^0$  allows the response times, the threshold voltage, the slope of the transmission characteristic lines etc. to be modified as desired. For example, 1E-alkenyl radicals, 3E-alkenyl radicals, 2E-alkenyloxy radicals and the like generally result in shorter response times, improved nematic tendencies and a higher ratio of the elastic constants  $k_{33}$  (bend) and  $k_{11}$  (splay) compared with alkyl or alkoxy radicals. 4-alkenyl radicals, 3-alkenyl radicals and the like generally result in lower threshold voltages and smaller values of  $k_{33}/k_{11}$  compared with alkyl and alkoxy radicals.

A  $-CH_2CH_2-$  group in  $Z^1$  generally results in higher values of  $k_{33}/k_{11}$  compared with a single covalent bond. Higher values of  $k_{33}/k_{11}$  facilitate, for example, flatter transmission characteristic lines in TN cells with a  $90^\circ$  twist (in order to achieve grey shades) and steeper transmission characteristic lines in STN, SBE and OMI cells (higher multiplexability), and vice versa.

The optimum weight ratio of compounds of the formulae I and II + III + IV + V + VI + VII + VIII + IX largely depends on the desired properties, on the choice of the components of the formulae I, II, III, IV, V, VI, VII, VIII, and/or IX, and on the choice of any other components which may be present. Suitable ratios within the range given above can easily be determined from case to case.

35

The total amount of compounds of the formulae I to XV in the mixtures according to the invention is not critical. The mixtures can therefore comprise one or more further components in order to optimize various

- 29 -

properties. However, the observed effect on the response times and the threshold voltage is usually greater the higher the total concentration of compounds of the formulae I to XV.

5

In a particularly preferred embodiment, the media according to the invention comprise compounds of the formulae II to IX (preferably II and/or III) in which  $X^0$  is  $OCF_3$ ,  $OCHF_2$ ,  $F$ ,  $OCH=CF_2$ ,  $OCF=CF_2$ ,  $OCF_2CHFCF_3$  or  $OCF_2-CF_2H$ . A favourable synergistic effect with the compounds of the formula I results in particularly advantageous properties.

The construction of the MLC display according to the invention from polarizers, electrode base plates and surface-treated electrodes corresponds to the conventional construction for displays of this type. The term conventional construction is broadly drawn here and also covers all variations and modifications of the MLC display, in particular including matrix display elements based on poly-Si TFT or MIM.

A significant difference between the displays according to the invention and the hitherto conventional displays based on the twisted nematic cell consists, however, in the choice of the liquid-crystal parameters of the liquid-crystal layer.

The liquid-crystal mixtures which can be used in accordance with the invention are prepared in a manner conventional per se. In general, the desired amount of the components used in a lesser amount is dissolved in the components making up the principal constituent, expediently at elevated temperature. It is also possible to mix solutions of the components in an organic solvent, for example in acetone, chloroform or methanol, and to remove the solvent again after thorough mixing, for example by distillation.

- 30 -

The dielectrics may also comprise further additives known to the person skilled in the art and described in the literature. For example, 0-15% of pleochroic dyes and/or chiral dopants can be added.

5

C denotes a crystalline phase, S a smectic phase, S<sub>c</sub> a smectic C phase, N a nematic phase and I the isotropic phase.

10 V<sub>10</sub> denotes the voltage for 10% transmission (viewing direction perpendicular to the plate surface). t<sub>on</sub> denotes the on and t<sub>off</sub> the off time at an operating voltage corresponding to 2.5 times the value of V<sub>10</sub>. Δn denotes the optical anisotropy and n<sub>0</sub> the refractive  
15 index. Δε denotes the dielectric anisotropy (Δε = ε<sub>||</sub> - ε<sub>⊥</sub>, where ε<sub>||</sub> refers to the dielectric constant parallel to the longitudinal axes of the molecule and ε<sub>⊥</sub> is the dielectric constant perpendicular thereto). The electro-optical data were measured in a TN cell in the  
20 1st minimum (i.e. at a d·Δn value of 0.5) at 20°C, unless expressly stated otherwise. The optical data were measured at 20°C, unless expressly stated otherwise.

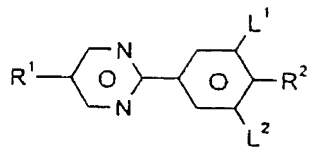
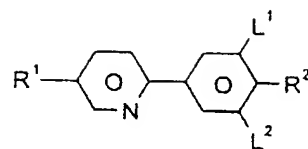
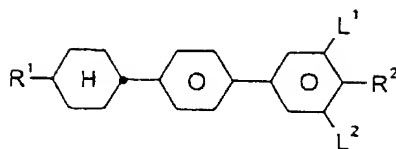
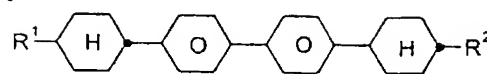
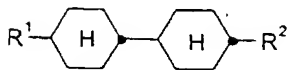
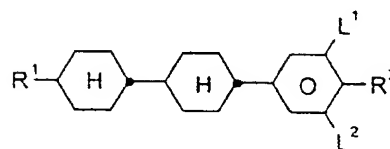
25 In the present application and in the following examples, the structures of the liquid-crystal compounds are specified by acronyms, which can be transformed into chemical formulae according to the following Tables A and B. All radicals C<sub>n</sub>H<sub>2n+1</sub> and C<sub>m</sub>H<sub>2m+1</sub>  
30 are straight-chain alkyl radicals having n or m carbon atoms. The coding according to Table B is self-evident. Table A specifies the acronym for the parent body only. In individual cases, the acronym for the parent body is followed, separated therefrom by a hyphen, by a code  
35 for the substituents R<sup>1</sup>, R<sup>2</sup>, L<sup>1</sup> and L<sup>2</sup>:

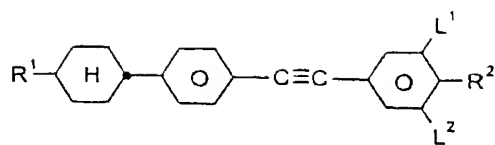
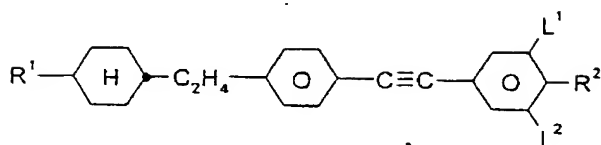
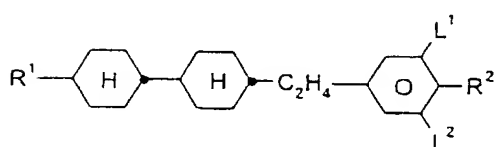
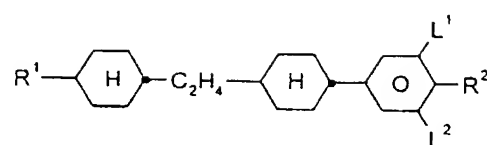
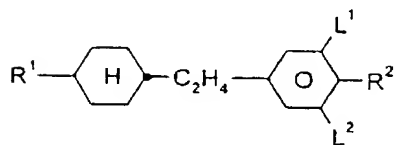
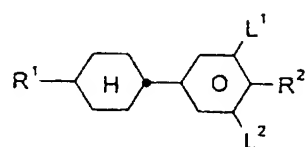
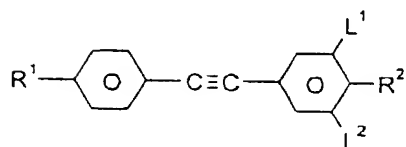
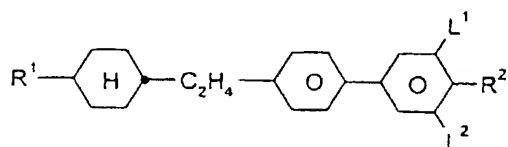
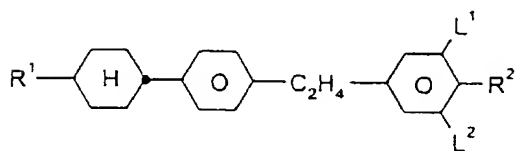
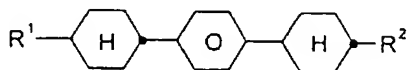
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Code for R <sup>1</sup> , R <sup>2</sup> , L <sup>1</sup> , L <sup>2</sup>		R <sup>2</sup>	L <sup>1</sup>	L <sup>2</sup>
nm	C <sub>n</sub> H <sub>2n+1</sub>	C <sub>m</sub> H <sub>2m+1</sub>	H	H
nOm	C <sub>n</sub> H <sub>2n+1</sub>	OC <sub>m</sub> H <sub>2m+1</sub>	H	H
nO.m	OC <sub>n</sub> H <sub>2n+1</sub>	C <sub>m</sub> H <sub>2m+1</sub>	H	H
n	C <sub>n</sub> H <sub>2n+1</sub>	CN	H	H
nN.F	C <sub>n</sub> H <sub>2n+1</sub>	CN	H	F
nF	C <sub>n</sub> H <sub>2n+1</sub>	F	H	H
nOF	OC <sub>n</sub> H <sub>2n+1</sub>	F	H	H
nCl	C <sub>n</sub> H <sub>2n+1</sub>	Cl	H	H
nF.F	C <sub>n</sub> H <sub>2n+1</sub>	F	H	F
nF.F.F	C <sub>n</sub> H <sub>2n+1</sub>	F	F	F
nCF <sub>3</sub>	C <sub>n</sub> H <sub>2n+1</sub>	CF <sub>3</sub>	H	H
nOCF <sub>3</sub>	C <sub>n</sub> H <sub>2n+1</sub>	OCF <sub>3</sub>	H	H
nOCF <sub>2</sub>	C <sub>n</sub> H <sub>2n+1</sub>	OCHF <sub>2</sub>	H	H
nS	C <sub>n</sub> H <sub>2n+1</sub>	NCS	H	H
rVsN	C <sub>r</sub> H <sub>2r+1</sub> -CH=CH-C <sub>s</sub> H <sub>2s</sub> -	CN	H	H
rEsN	C <sub>r</sub> H <sub>2r+1</sub> -O-C <sub>2</sub> H <sub>2s</sub> -	CN	H	H
nAm	C <sub>n</sub> H <sub>2n+1</sub>	COOC <sub>m</sub> H <sub>2m+1</sub>	H	H
nOCCF <sub>2</sub> .F.F	C <sub>n</sub> H <sub>2n+1</sub>	OCH <sub>2</sub> CF <sub>2</sub> H	F	F

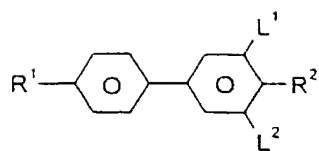
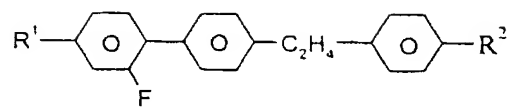
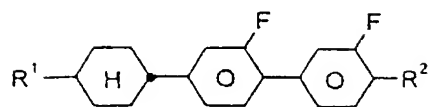
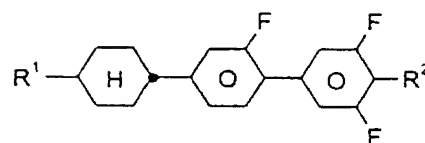
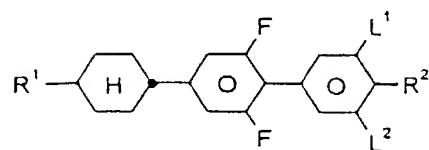
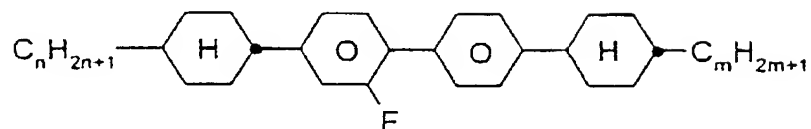
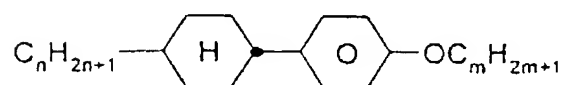
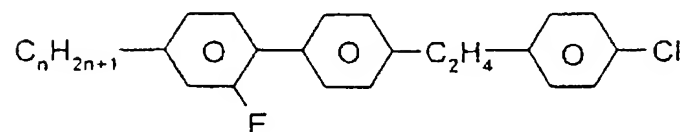
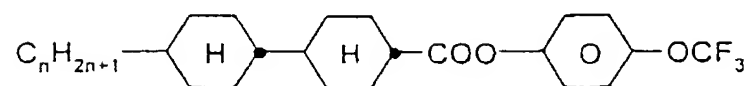
5 Preferred mixture components are shown in Tables A and B.

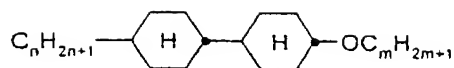
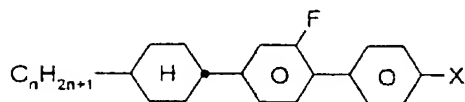
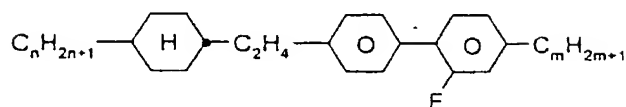
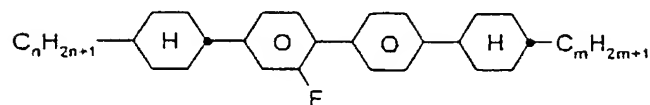
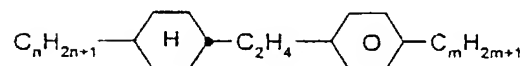
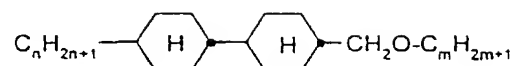
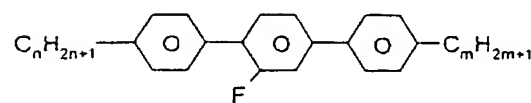
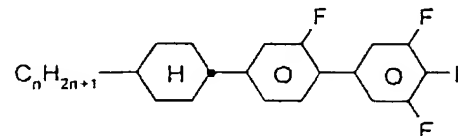
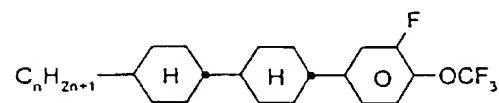
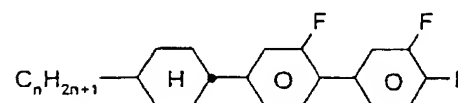


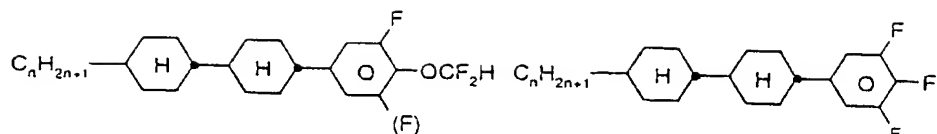
Table A:**PYP****PYRP****BCH****CBC****CCH****CCP**

**CPTP****CEPTP****ECCP****CECP****EPCH****PCH****PTP****BECH****EBCH****CPC**

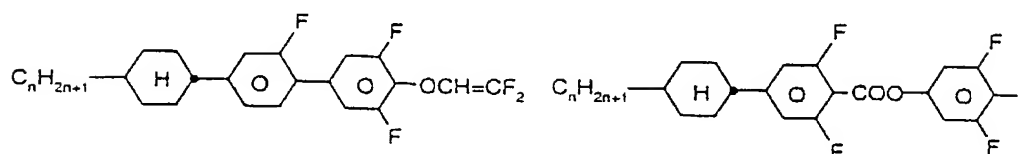
- 34 -

**B****FET-nF****CGG****CGU****CUP**Table B:**CBC-nmF****PCH-nOm****FET-nCl****CP-nOCF₃**

**CCH-nOm****BCH-n.Fm****Inm****CBC-nmF****ECCP-nm****CCH-n1EM****T-nFm****CGU-n-F****CCP-nOCF<sub>3</sub>.F****CGG-n-F**

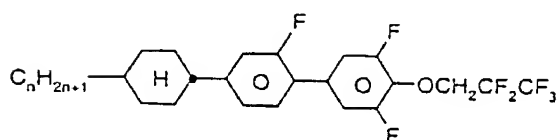
CCP-nOCF<sub>2</sub>.F(F)

CCP-nF.F.F

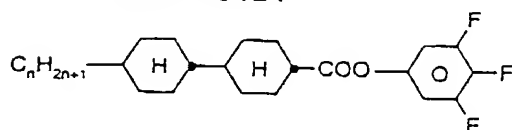


CGU-n-OXF

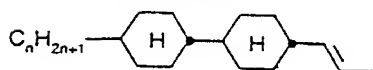
CUZU-n-F



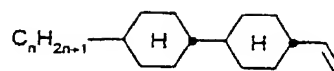
CGU-n-O1DT



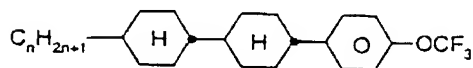
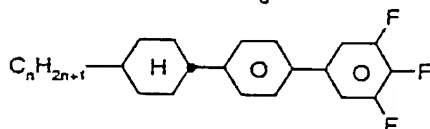
CCZU-n-F



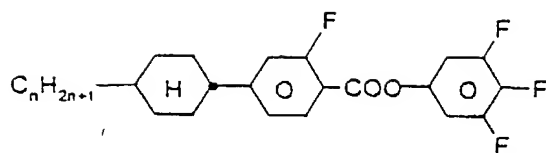
CC-n-V1



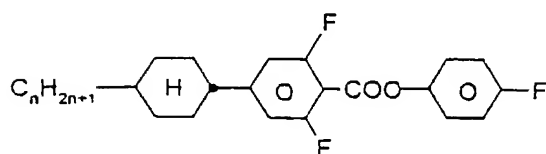
CC-n-V

CCP-nOCF<sub>3</sub>

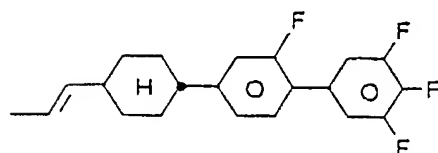
BCH-nF.F.F



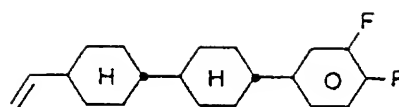
CGZU-n-F



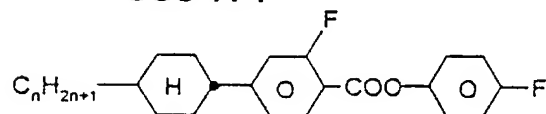
CUZP-n-F



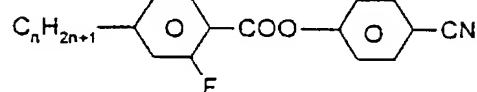
CGU-1V-F



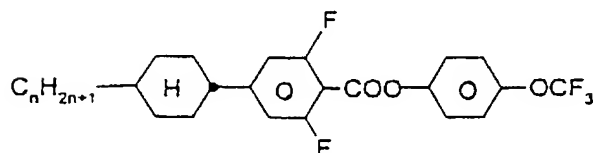
CCG-V-F



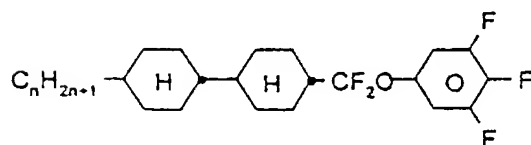
CGZP-n-F



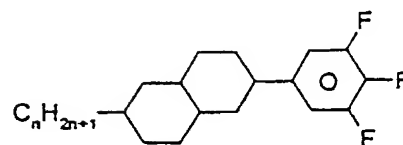
UZP-n-N



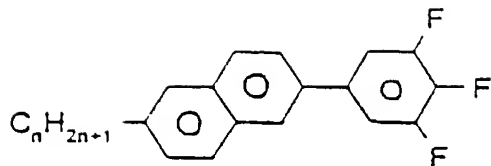
CUZP-n-OT



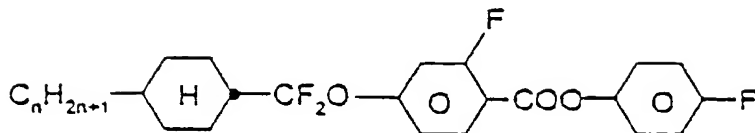
CCQU-n-F



Dec-U-n-F



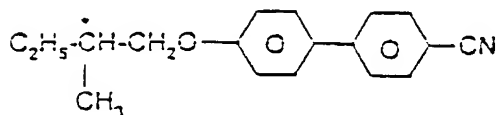
**Nap-U-n-F**



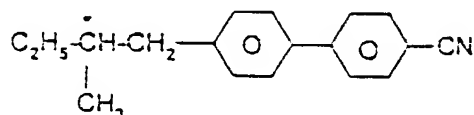
**CQGZP-n-F**

Table C:

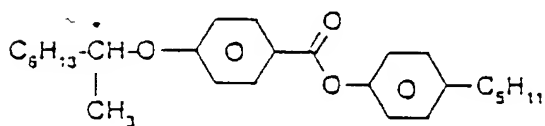
- 5 Table C specifies possible dopants which are generally added to the mixtures according to the invention.



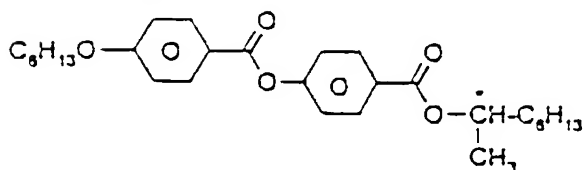
**C 15**



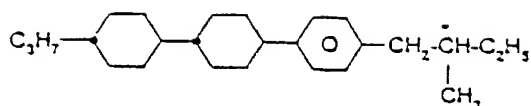
**CB 15**



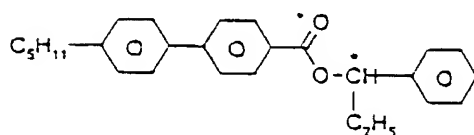
**CM 21**



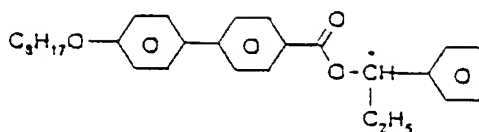
**R/S 811**



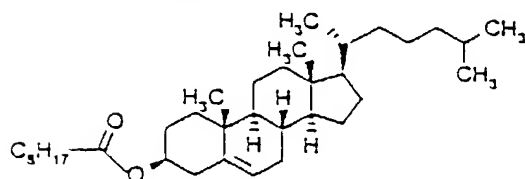
CM 44



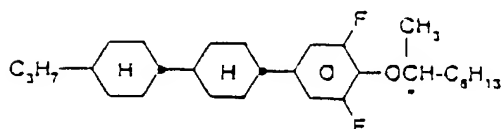
CM 45



CM 47



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R/S 2011

The following examples are intended to illustrate the invention without limiting it. Hereinbefore and hereinafter, percentages are given in per cent by weight. All temperatures are specified in degrees Celsius. m.p. denotes melting point, cl.p. denotes clearing point. Furthermore, C = crystalline state, N = nematic phase, S = smectic phase and I = isotropic phase. The data between these symbols represent the transition temperatures.  $\Delta n$  denotes the optical anisotropy (589 nm, 20°C), and the flow viscosity (mm<sup>2</sup>/sec) and the rotational viscosity  $\gamma_1$  (mPa·s) were each determined at 20°C.

Conventional work-up means that water is added if necessary, the mixture is extracted with

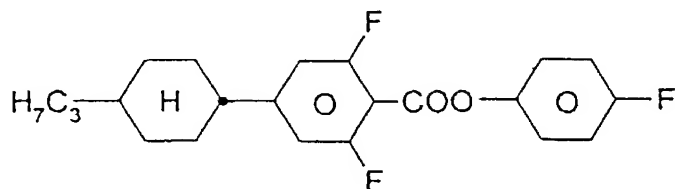


- 40 -

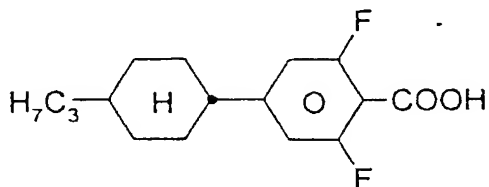
dichloromethane, diethyl ether, methyl tert-butyl ether or toluene, the organic phase is separated off, dried and evaporated, and the product is purified by distillation under reduced pressure or crystallization and/or chromatography. The following abbreviations are used:

n-BuLi      1.6 molar solution of n-butyllithium in n-hexane  
 10 DMAP        4-(dimethylamino)pyridine  
 THF         tetrahydrofuran  
 DCC         N,N'-dicyclohexylcarbodiimide

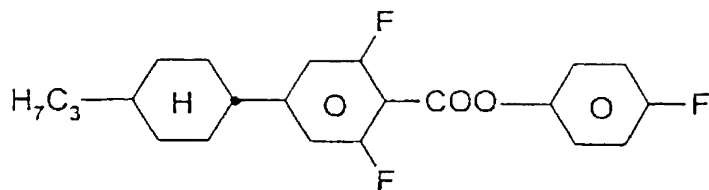
### Example 1



### Step 1.1



1.32 mol of n-butyllithium (15% in n-hexane) are added dropwise over the course of 1 h to 1.2 mol of 4-(trans-4-propylcyclohexyl)-2,6-difluorobenzoic acid in 3 l THF at -70°C in a nitrogen atmosphere. Stirring is continued for 1 h, crushed dry ice is added at -70°C, and stirring is continued for a further 1.5 h. 3 l of water are added, the organic phase is separated off and the aqueous phase is extracted with toluene. The combined organic extracts are then subjected to conventional work-up.

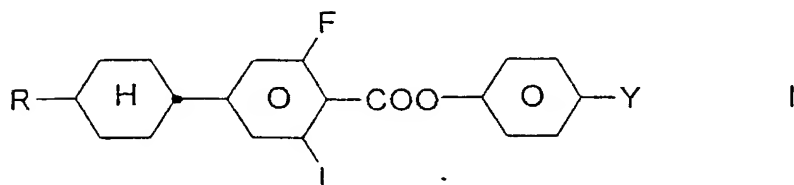
Step 1.2

5 A solution of 0.11 mol of DCC in 50 ml of toluene is added dropwise to 0.1 mol of 4-(trans-4-propylcyclohexyl)-2,6-difluorobenzoic acid, 0.1 mol of 4-fluorophenol and 0.004 mol of DMAP in 200 ml of toluene at 10°C. The mixture is stirred for 48 h at  
 10 room temperature and then admixed with 0.016 mol of oxalic acid dihydrate. After stirring further for 1 h, solid constituents are separated off and the solution is subjected to conventional work-up.

K 63 N 106.6 I;  $\Delta n = +0.113$ ;  $\Delta \epsilon = +13.72$ .


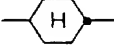
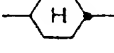
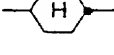
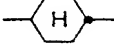
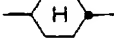
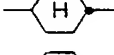
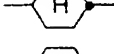

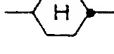
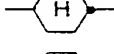
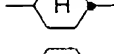

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The following compounds of the formula I



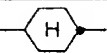


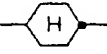
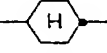
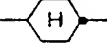
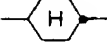
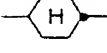
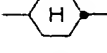
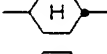
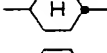
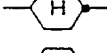
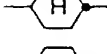
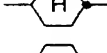
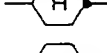
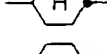





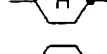
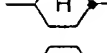
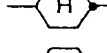
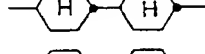
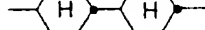
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are prepared in a similar manner:

R	$-(A'-Z')_m-$	L	Y
CH <sub>3</sub>		H	F
CH <sub>3</sub>		F	F
C <sub>2</sub> H <sub>5</sub>		H	F
C <sub>2</sub> H <sub>5</sub>		F	F
K 52 N 72.2 I; $\Delta\epsilon = 12.65$ ; $\Delta n = 0.109$			
n-C <sub>3</sub> H <sub>7</sub>		H	F
n-C <sub>4</sub> H <sub>9</sub>		H	F
n-C <sub>4</sub> H <sub>9</sub>		F	F
n-C <sub>5</sub> H <sub>11</sub>		H	F
n-C <sub>5</sub> H <sub>11</sub>		F	F
K 57 N 111.3 I; $\Delta\epsilon = 11.8$ ; $\Delta n = 0.084$			
n-C <sub>6</sub> H <sub>13</sub>		H	F
n-C <sub>6</sub> H <sub>13</sub>		F	F
CH <sub>2</sub> =CH		H	F
CH <sub>2</sub> CH		F	F

R	-(A'-Z') <sub>m</sub> -	L	Y	
CH <sub>2</sub> CH		H	F	
CH <sub>3</sub> CH=CH		F	F	
CH <sub>2</sub> =CHCH <sub>2</sub>		H	F	
CH <sub>2</sub> =CHCH <sub>2</sub>		F	F	
CH <sub>2</sub> =CHC <sub>2</sub> H <sub>4</sub>		H	F	
CH <sub>2</sub> =CHC <sub>2</sub> H <sub>4</sub>		F	F	
CH <sub>3</sub> CH=CHCH <sub>2</sub>		H	F	
CH <sub>3</sub> CH=CHCH <sub>2</sub>		F	F	
CH <sub>3</sub> CH=CHC <sub>2</sub> H <sub>4</sub>		H	F	
CH <sub>3</sub> CH=CHC <sub>2</sub> H <sub>4</sub>		F	F	
C <sub>2</sub> H <sub>5</sub> O		H	F	
C <sub>2</sub> H <sub>5</sub> O		F	F	
CH <sub>3</sub>		H	OCF <sub>3</sub>	
CH <sub>3</sub>		F	OCF <sub>3</sub>	
C <sub>2</sub> H <sub>5</sub>		H	OCF <sub>3</sub>	K 55 S <sub>A</sub> 77 N 127.9 I; Δε = 16.38; Δn = 0.127
C <sub>2</sub> H <sub>5</sub>		F	OCF <sub>3</sub>	
n-C <sub>3</sub> H <sub>7</sub>		H	OCF <sub>3</sub>	K 64 S <sub>A</sub> 100 N 151.4 I; Δε = 15.97; Δn = 0.136
n-C <sub>3</sub> H <sub>7</sub>		F	OCF <sub>3</sub>	
n-C <sub>4</sub> H <sub>9</sub>		H	OCF <sub>3</sub>	
n-C <sub>4</sub> H <sub>9</sub>		F	OCF <sub>3</sub>	
n-C <sub>5</sub> H <sub>11</sub>		H	OCF <sub>3</sub>	

R	$-(A^1-Z^1)_m-$	L	Y
$n-C_5H_{11}$		F	$OCF_3$
$n-C_6H_{13}$		H	$OCF_3$
$n-C_6H_{13}$		F	$OCF_3$
$CH_2=CH$		H	$OCF_3$
$CH_2CH$		F	$OCF_3$
$CH_2CH$		H	$OCF_3$
$CH_3CH=CH$		F	$OCF_3$
$CH_2=CHCH_2$		H	$OCF_3$
$CH_2=CHCH_2$		F	$OCF_3$
$CH_2=CHC_2H_5$		H	$OCF_3$
$CH_2=CHC_2H_5$		F	$OCF_3$
$CH_3CH=CHCH_2$		H	$OCF_3$
$CH_3CH=CHCH_2$		F	$OCF_3$
$CH_3CH=CHC_2H_5$		H	$OCF_3$
$CH_3CH=CHC_2H_5$		F	$OCF_3$
$C_2H_5O$		H	$OCF_3$
$C_2H_5O$		F	$OCF_3$
$CH_3$		H	$OCHF_2$
$CH_3$		F	$OCHF_2$
$C_2H_5$		H	$OCHF_2$
$C_2H_5$		F	$OCHF_2$
$n-C_3H_7$		H	$OCHF_2$

R	$-(A^1-Z^1)_m-$	L	Y
$n-C_4H_9$		H	OCHF <sub>2</sub>
$n-C_4H_9$		F	OCHF <sub>2</sub>
$n-C_5H_{11}$		H	OCHF <sub>2</sub>
$n-C_5H_{11}$		F	OCHF <sub>2</sub>
$n-C_6H_{13}$		H	OCHF <sub>2</sub>
$n-C_6H_{13}$		F	OCHF <sub>2</sub>
CH <sub>2</sub> =CH		H	OCHF <sub>2</sub>
CH <sub>2</sub> CH		F	OCHF <sub>2</sub>
CH <sub>2</sub> CH		H	OCHF <sub>2</sub>
CH <sub>3</sub> CH=CH		F	OCHF <sub>2</sub>
CH <sub>2</sub> =CHCH <sub>2</sub>		H	OCHF <sub>2</sub>
CH <sub>2</sub> =CHCH <sub>2</sub>		F	OCHF <sub>2</sub>
CH <sub>2</sub> =CHC <sub>2</sub> H <sub>4</sub>		H	OCHF <sub>2</sub>
CH <sub>2</sub> =CHC <sub>2</sub> H <sub>4</sub>		F	OCHF <sub>2</sub>
CH <sub>3</sub> CH=CHCH <sub>2</sub>		H	OCHF <sub>2</sub>
CH <sub>3</sub> CH=CHCH <sub>2</sub>		F	OCHF <sub>2</sub>
CH <sub>3</sub> CH=CHC <sub>2</sub> H <sub>4</sub>		H	OCHF <sub>2</sub>
CH <sub>3</sub> CH=CHC <sub>2</sub> H <sub>4</sub>		F	OCHF <sub>2</sub>
C <sub>2</sub> H <sub>5</sub> O		H	OCHF <sub>2</sub>
C <sub>2</sub> H <sub>5</sub> O		F	OCHF <sub>2</sub>
$n-C_3H_7$		F	OCHF <sub>2</sub> CF <sub>3</sub>
$n-C_3H_7$		F	OCF <sub>2</sub> CHFCF <sub>3</sub>
CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub>		H	CF <sub>3</sub>
$n-C_5H_{11}$		F	CN
$n-C_5H_{11}$		H	OCF <sub>3</sub>
$n-C_5H_{11}$		F	F

## Mixture examples

### Example M1

CCH-34	5.00%	S→N [°C]: < -40.0
CC-3-V1	4.00%	Clearing point [°C]: +70.5
CCP-2F.F.F	11.00%	Δn [589 nm, 20°C]: +0.0901
CCP-3F.F.F	10.00%	γ <sub>1</sub> [20°C; mPa·s]: 151
CCP-30CF <sub>3</sub>	1.00%	
CGU-2-F	11.00%	
CGU-3-F	11.00%	
CGU-5-F	6.00%	
CCZU-2-F	5.00%	
CCZU-3-F	15.00%	
CCZU-5-F	5.00%	
CGZP-2-OT	10.00%	
CGZP-3-OT	6.00%	

5

### Example M2

CC-3-V1	3.00%	S→N [°C]: < -40.0
CCH-34	6.00%	Clearing point [°C]: +70.0
CCP-2F.F.F	11.00%	Δn [589 nm, 20°C]: +0.0904
CCP-3F.F.F	12.00%	γ <sub>1</sub> [20°C; mPa·s]: 149
CGU-2-F	11.00%	
CGU-3-F	11.00%	
CGU-5-F	5.00%	
CCZU-2-F	5.00%	
CCZU-3-F	15.00%	
CCZU-5-F	3.00%	
CGZP-2-OT	10.00%	
CGZP-3-OT	8.00%	

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Example M3

CC-3-V1	5.00%	S→N [°C]: < -40.0
CCH-34	6.00%	Clearing point [°C]: +70.5
CCP-2F.F.F	10.00%	$\Delta n$ [589 nm, 20°C]: +0.0910
CCP-3F.F.F	10.00%	$\Delta \epsilon$ [1 kHz; 20°C]: 4.8
CGU-2-F	11.00%	$\gamma_1$ [20°C; mPa·s]: 145
CGU-3-F	11.00%	
CGU-5-F	6.00%	
CCZU-2-F	5.00%	
CCZU-3-F	15.00%	
CCZU-5-F	3.00%	
CGZP-2-OT	10.00%	
CGZP-3-OT	8.00%	

Example M4

5

CC-3-V1	5.00%	S→N [°C]: < -40.0
CCH-34	6.00%	Clearing point [°C]: +71.0
CCP-2F.F.F	10.00%	$\Delta n$ [589 nm, 20°C]: +0.0905
CCP-3F.F.F	9.50%	$\Delta \epsilon$ [1 kHz; 20°C]: 4.8
CCP-20CF <sub>3</sub>	1.00%	$\gamma_1$ [20°C; mPa·s]: 144
CGU-2-F	11.00%	
CGU-3-F	11.00%	
CGU-5-F	5.50%	
CCZU-2-F	5.00%	
CCZU-3-F	15.00%	
CCZU-5-F	3.00%	
CGZP-2-OT	11.00%	
CGZP-3-OT	7.00%	



Example M5

CC-3-V1	5.00%
CCH-34	6.00%
CCP-2F.F.F	11.00%
CCP-3F.F.F	9.00%
CCP-20CF <sub>3</sub>	1.00%
CGU-2-F	11.00%
CGU-3-F	11.00%
CGU-5-F	5.00%
CCZU-2-F	5.00%
CCZU-3-F	15.00%
CCZU-5-F	3.00%
CGZP-2-OT	11.00%
CGZP-3-OT	7.00%

Example M6

5

CC-3-V1	7.00%
CCH-34	6.00%
CCP-2F.F.F	11.00%
CCP-3F.F.F	7.00%
CGU-2-F	11.00%
CGU-3-F	11.00%
CGU-5-F	5.00%
CCZU-2-F	5.00%
CCZU-3-F	15.00%
CCZU-5-F	3.00%
CGZP-2-OT	11.00%
CGZP-3-OT	8.00%

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Example M7

CC-3-V1	5.00%
CCH-34	6.00%
CCP-2F.F.F	10.50%
CCP-3F.F.F	9.50%
CGU-2-F	11.00%
CGU-3-F	11.00%
CGU-5-F	5.00%
CCZU-2-F	5.00%
CCZU-3-F	15.00%
CCZU-5-F	4.00%
CGZP-2-OT	11.00%
CGZP-3-OT	7.00%

Clearing point [°C]: +71.0  
 $\Delta n$  [589 nm, 20°C]: +0.0904

Example M8

5

CC-3-V1	5.00%
CCH-34	6.00%
CCP-2F.F.F	9.00%
CCP-3F.F.F	11.00%
CGU-2-F	11.00%
CGU-3-F	11.00%
CGU-5-F	6.00%
CCZU-2-F	5.00%
CCZU-3-F	15.00%
CCZU-5-F	3.00%
CGZP-2-OT	11.00%
CGZP-3-OT	7.00%

Clearing point [°C]: +71.0  
 $\Delta n$  [589 nm, 20°C]: +0.0908

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Example M9

CC-3-V1	3.00%	S→N [°C]: < -40.0
CCP-2F.F.F	10.00%	Clearing point [°C]: +71.5
CCP-3F.F.F	10.00%	$\Delta n$ [589 nm, 20°C]: +0.0908
CCP-20CF <sub>3</sub> .F	8.00%	$\gamma_1$ [20°C; mPa·s]: 167
CCP-40CF <sub>3</sub>	5.00%	
CGU-2-F	11.00%	
CGU-3-F	11.00%	
CGU-5-F	7.00%	
CCZU-2-F	5.00%	
CCZU-3-F	15.00%	
CCZU-5-F	5.00%	
CGZP-2-OT	5.00%	
CGZP-3-OT	5.00%	

Example M10

5

BCH-32	3.00%	S→N [°C]: < -40.0
CC-3-V1	3.00%	Clearing point [°C]: +70.0
CCP-2F.F.F	6.00%	$\Delta n$ [589 nm, 20°C]: +0.1046
CCP-30CF <sub>3</sub>	5.00%	$\gamma_1$ [20°C; mPa·s]: 173
CGU-2-F	11.00%	
CGU-3-F	10.00%	
CGU-5-F	6.00%	
CCZU-2-F	5.00%	
CCZU-3-F	15.00%	
CCZU-5-F	5.00%	
BCH-3F.F.F	13.00%	
BCH-5F.F.F	9.00%	
CGZP-2-OT	2.00%	
CGZP-3-OT	7.00%	

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Example M11

CC-3-V1	3.00%	S→N [°C]: < -40.0
CCP-2F.F.F	10.00%	Clearing point [°C]: +70.5
CCP-3F.F.F	11.00%	$\Delta n$ [589 nm, 20°C]: +0.0902
CCP-20CF <sub>3</sub> .F	8.00%	$\gamma_1$ [20°C; mPa·s]: 166
CCP-40CF <sub>3</sub>	4.00%	
CGU-2-F	11.00%	
CGU-3-F	11.00%	
CGU-5-F	7.00%	
CCZU-2-F	5.00%	
CCZU-3-F	15.00%	
CCZU-5-F	5.00%	
CGZP-2-OT	6.00%	
CGZP-3-OT	4.00%	

Example M12

5

BCH-32	3.00%	S→N [°C]: < -40.0
CC-3-V1	3.00%	Clearing point [°C]: +70.5
CCP-2F.F.F	5.00%	$\Delta n$ [589 nm, 20°C]: +0.1050
CCP-30CF <sub>3</sub>	5.00%	$\gamma_1$ [20°C; mPa·s]: 174
CGU-2-F	10.00%	
CGU-3-F	11.00%	
CGU-5-F	6.00%	
CCZU-2-F	5.00%	
CCZU-3-F	15.00%	
CCZU-5-F	5.00%	
BCH-3F.F.F	13.00%	
BCH-5F.F.F	10.00%	
CGZP-2-OT	3.00%	
CGZP-3-OT	6.00%	

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Example M13

CCH-34	6.00%	S→N [°C]: < -40.0
CC-3-V1	2.00%	Clearing point [°C]: +70.0
CCP-2F.F.F	11.00%	Δn [589 nm, 20°C]: +0.0895
CCP-3F.F.F	12.00%	
CCP-20CF <sub>3</sub>	1.00%	
CGU-2-F	11.00%	
CGU-3-F	5.00%	
CGU-5-F	5.00%	
CCZU-2-F	15.00%	
CCZU-3-F	5.00%	
CCZU-5-F	10.00%	
CGZP-2-OT	6.00%	
CGZP-3-OT		

Example M14

5

CC-3-V1	4.00%	S→N [°C]: < -40.0
CCH-34	3.00%	Clearing point [°C]: +70.5
CCP-2F.F.F	10.00%	Δn [589 nm, 20°C]: +0.0909
CCP-3F.F.F	7.00%	γ <sub>1</sub> [20°C; mPa·s]: 147
CCP-30CF <sub>3</sub>	5.00%	Twist: 90°
CGU-2-F	11.00%	d·Δn [μm]: 0.50
CGU-3-F	11.00%	V <sub>(10,0,20)</sub> [V]: 1.00
CGU-5-F	2.00%	
CCZU-2-F	5.00%	
CCZU-3-F	15.00%	
CCZU-5-F	3.00%	
CUZP-2-OT	13.00%	
CUZP-3-OT	11.00%	

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Example M15

CC-3-V1	4.00%	S→N [°C]: < -40.0
CCH-34	4.00%	Clearing point [°C]: +71.0
CCP-2F.F.F	10.00%	$\Delta n$ [589 nm, 20°C]: +0.0920
CCP-3F.F.F	4.00%	Twist: 90°
BCH-2F.F.F	3.00%	$d \cdot \Delta n$ [ $\mu m$ ]: 0.50
CCP-20CF <sub>3</sub>	4.00%	$V_{(10,0,20)}$ [V]: 1.00
CGU-2-F	10.00%	
CGU-3-F	10.00%	
CGU-5-F	2.00%	
CCZU-2-F	5.00%	
CCZU-3-F	15.00%	
CCZU-5-F	3.00%	
CUZP-2-OT	10.00%	
CUZP-3-OT	8.00%	
CUZP-5-OT	8.00%	

Example M16

5

CC-3-V1	2.00%	S→N [°C]: < -40.0
CCH-34	5.00%	Clearing point [°C]: +70.5
CCP-2F.F.F	9.00%	$\Delta n$ [589 nm, 20°C]: +0.0900
CCP-3F.F.F	9.00%	$\gamma_1$ [20°C; mPa·s]: 148
CCP-30CF <sub>3</sub>	4.00%	Twist: 90°
CGU-2-F	11.00%	$d \cdot \Delta n$ [ $\mu m$ ]: 0.50
CGU-3-F	11.00%	$V_{(10,0,20)}$ [V]: 0.98
CGU-5-F	2.00%	
CCZU-2-F	5.00%	
CCZU-3-F	15.00%	
CCZU-5-F	4.00%	
CUZP-2-OT	12.00%	
CUZP-3-OT	11.00%	

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Example M17

CCH-34	5.00%	S→N [°C]: < -40.0
CCP-2F.F.F	11.00%	Clearing point [°C]: +72.0
CCP-3F.F.F	11.00%	$\Delta n$ [589 nm, 20°C]: +0.0954
CCP-20CF <sub>3</sub> .F	10.00%	$\gamma_1$ [20°C; mPa·s]: 154
CCP-30CF <sub>3</sub>	5.00%	Twist: 90°
CCP-40CF <sub>3</sub>	5.00%	$d \cdot \Delta n$ [μm]: 0.50
CGU-2-F	10.00%	$V_{(10,0,20)}$ [V]: 1.09
CGU-3-F	10.00%	
CGU-5-F	4.00%	
CPZG-2-OT	2.00%	
CPZG-3-OT	4.00%	
CUZP-2-OT	12.00%	
CUZP-3-OT	10.00%	
CBC-33	1.00%	

Example M18

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CCP-2F.F.F	10.00%	S→N [°C]: < -40.0
CCP-3F.F.F	11.00%	Clearing point [°C]: +70.5
BCH-3F.F.F	5.00%	$\Delta n$ [589 nm, 20°C]: +0.0944
CCP-30CF <sub>3</sub>	9.00%	$\gamma_1$ [20°C; mPa·s]: 169
CGU-2-F	10.00%	Twist: 90°
CGU-3-F	10.00%	$d \cdot \Delta n$ [μm]: 0.50
CGU-5-F	3.00%	$V_{(10,0,20)}$ [V]: 0.98
CCZU-2-F	4.00%	
CCZU-3-F	14.00%	
CCZU-5-F	2.00%	
CUZP-2-OT	12.00%	
CUZP-3-OT	10.00%	

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Example M19

CCH-34	2.00%	S→N [°C]: < -40.0
CCP-2F.F.F	10.00%	Clearing point [°C]: +72.0
CCP-3F.F.F	12.00%	$\Delta n$ [589 nm, 20°C]: +0.0908
CCP-20CF <sub>3</sub>	5.00%	$\gamma_1$ [20°C; mPa·s]: 162
CCP-30CF <sub>3</sub>	3.00%	Twist: 90°
CGU-2-F	10.00%	$d \cdot \Delta n$ [μm]: 0.50
CGU-2-F	11.00%	$V_{(10,0,20)}$ [V]: 0.95
CCZU-2-F	5.00%	
CCZU-3-F	15.00%	
CCZU-5-F	3.00%	
CUZP-2-OT	13.00%	
CUZP-3-OT	11.00%	

Example M20

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CC-3-VI	4.00%	S→N [°C]: < -40.0
CCP-2F.F.F	11.00%	Clearing point [°C]: +70.0
CCP-3F.F.F	11.00%	$\Delta n$ [589 nm, 20°C]: +0.0900
CCP-20CF <sub>3</sub>	6.00%	$\gamma_1$ [20°C; mPa·s]: 154
CGU-2-F	10.00%	Twist: 90°
CGU-3-F	11.00%	$d \cdot \Delta n$ [μm]: 0.50
CCZU-2-F	5.00%	$V_{(10,0,20)}$ [V]: 0.96
CCZU-3-F	15.00%	
CCZU-5-F	3.00%	
CUZP-2-OT	13.00%	
CUZP-3-OT	11.00%	



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Example M21

CCH-34	3.00%	S→N [°C]: < -40.0
CCP-2F.F.F	11.00%	Clearing point [°C]: +70.5
CCP-3F.F.F	12.00%	$\Delta n$ [589 nm, 20°C]: +0.0900
CCP-20CF <sub>3</sub>	5.00%	$\gamma_1$ [20°C; mPa·s]: 154
CCP-30CF <sub>3</sub>	4.00%	Twist: 90°
CGU-2-F	11.00%	$d \cdot \Delta n$ [ $\mu\text{m}$ ]: 0.50
CGU-3-F	10.00%	$V_{(10,0,20)}$ [V]: 0.97
CCZU-2-F	5.00%	
CCZU-3-F	15.00%	
CUZP-2-OT	13.00%	
CUZP-3-OT	11.00%	

Example M22

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CC-3-V1	5.00%	S→N [°C]: < -40.0
CCP-2F.F.F	10.00%	Clearing point [°C]: +70.0
CCP-3F.F.F	12.00%	$\Delta n$ [589 nm, 20°C]: +0.0892
CCP-30CF <sub>3</sub>	9.00%	$\gamma_1$ [20°C; mPa·s]: 154
CGU-2-F	11.00%	Twist: 90°
CGU-3-F	11.00%	$d \cdot \Delta n$ [ $\mu\text{m}$ ]: 0.50
CGU-5-F	3.00%	$V_{(10,0,20)}$ [V]: 0.99
CCZU-2-F	5.00%	
CCZU-3-F	15.00%	
CCZU-5-F	4.00%	
CUZP-2-F	11.00%	
CUZP-3-F	4.00%	

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Example M23

CCH-34	5.00%	S→N [°C]: < -40.0
CCP-2F.F.F	11.00%	Clearing point [°C]: +69.0
CCP-3F.F.F	11.00%	$\Delta n$ [589 nm, 20°C]: +0.0958
CCP-20CF <sub>3</sub> .F	6.00%	$\gamma_1$ [20°C; mPa·s]: 159
CCP-30CF <sub>3</sub>	6.00%	Twist: 90°
CCP-40CF <sub>3</sub>	5.00%	d· $\Delta n$ [μm]: 0.50
CGU-2-F	11.00%	$V_{(10,0,20)}$ [V]: 0.96
CGU-3-F	11.00%	
CGU-5-F	5.00%	
CPZG-2-OT	3.00%	
CPZG-3-OT	5.00%	
CUZP-2-F	10.00%	
CUZP-3-F	10.00%	
CBC-33	1.00%	

Example M24

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BCH-32	3.00%	S→N [°C]: < -40.0
CCP-2F.F.F	11.00%	Clearing point [°C]: +65.0
CCP-3F.F.F	9.00%	$\Delta n$ [589 nm, 20°C]: +0.0940
BCH-3F.F.F	6.00%	Twist: 90°
CCP-30CF <sub>3</sub>	7.00%	d· $\Delta n$ [μm]: 0.50
CGU-2-F	11.00%	$V_{(10,0,20)}$ [V]: 0.96
CGU-3-F	11.00%	
CGU-5-F	7.00%	
CCZU-2-F	5.00%	
CCZU-3-F	15.00%	
CCZU-5-F	5.00%	
CUZP-2-F	10.00%	

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Example M25

BCH-32	5.00%	S→N [°C]: < -40.0
CCP-2F.F.F	11.00%	Clearing point [°C]: +70.0
CCP-3F.F.F	11.00%	$\Delta n$ [589 nm, 20°C]: +0.0946
BCH-3F.F.F	3.00%	Twist: 90°
CCP-30CF <sub>3</sub>	8.00%	$d \cdot \Delta n$ [μm]: 0.50
CGU-2-F	11.00%	$V_{(10,0,20)}$ [V]: 1.00
CGU-3-F	11.00%	
CGU-5-F	5.00%	
CCZU-2-F	5.00%	
CCZU-3-F	15.00%	
CCZU-5-F	5.00%	
CUZP-2-F	10.00%	

Example M26

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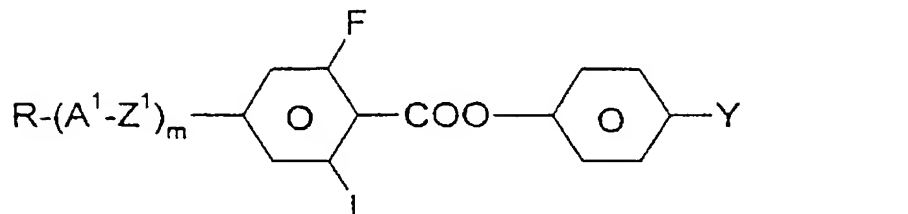
CCH-34	2.00%	S→N [°C]: < -40.0
BCH-32	2.00%	Clearing point [°C]: +71.5
CCP-2F.F.F	10.00%	$\Delta n$ [589 nm, 20°C]: +0.0907
CCP-3F.F.F	12.00%	$\gamma_1$ [20°C; mPa·s]: 166
CCP-30CF <sub>3</sub>	9.00%	Twist: 90°
CGU-2-F	11.00%	$d \cdot \Delta n$ [μm]: 0.50
CGU-3-F	11.00%	$V_{(10,0,20)}$ [V]: 0.99
CGU-5-F	3.00%	
CCZU-2-F	5.00%	
CCZU-3-F	15.00%	
CCZU-5-F	5.00%	
CUZP-2-F	11.00%	
CUZP-3-F	4.00%	

Example M27

CCH-34	3.00%
BCH-32	2.00%
CCP-2F.F.F	11.00%
CCP-3F.F.F	12.00%
CCP-30CF <sub>3</sub>	9.00%
CGU-2-F	11.00%
CGU-3-F	11.00%
CGU-5-F	3.00%
CCZU-2-F	5.00%
CCZU-3-F	15.00%
CCZU-5-F	3.00%
CUZP-2-F	11.00%
CUZP-3-F	4.00%

## Patent Claims

1. Liquid-crystalline phenol esters of the formula I



5 in which

R is H, an alkyl or alkenyl radical having up to 15 carbon atoms which is unsubstituted, monosubstituted by CN or CF<sub>3</sub>, or at least monosubstituted by halogen, where one or more CH<sub>2</sub> groups in these radicals may also be replaced by -O-, -S-, -C≡C-, -OC-O- or -O-CO- in such a way that O atoms are not linked directly to one another,

15

A<sup>1</sup> a) is a 1,4-cyclohexenylenyl or 1,4-cyclohexenylenyl radical, in which one or two non-adjacent CH<sub>2</sub> groups may be replaced by -O- or -S-,

20

b) is a 1,4-phenylenyl radical, in which one or two CH groups may be replaced by N,

25

c) is a piperidine-1,4-diyl, 1,4-bicyclo[2.2.2]octylenyl, naphthalene-2,6-diyl, decahydronaphthalene-2,6-diyl or 1,2,3,4-tetrahydronaphthalene-2,6-diyl radical,

30

where the radicals a), b) and c) may be monosubstituted or polysubstituted by halogen atoms,

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$Z^1$  is  $-\text{CO}-\text{O}-$ ,  $-\text{O}-\text{CO}-$ ,  $-\text{CF}_2\text{O}-$ ,  $-\text{OCF}_2-$ ,  $-\text{CH}_2\text{O}-$ ,  
 $-\text{OCH}_2-$ ,  $-\text{CH}_2\text{CH}_2-$ ,  $-\text{C}_2\text{F}_4-$ ,  $-\text{CH}=\text{CH}-$ ,  $-\text{C}\equiv\text{C}-$  or a  
 single bond,

5 Y is F, Cl, CN or a monohalogenated or  
 polyhalogenated alkyl, alkenyl, alkenyloxy or  
 alkoxy radical having 1 to 5 carbon atoms,

L is H or F, and

10

m is 0, 1 or 2.

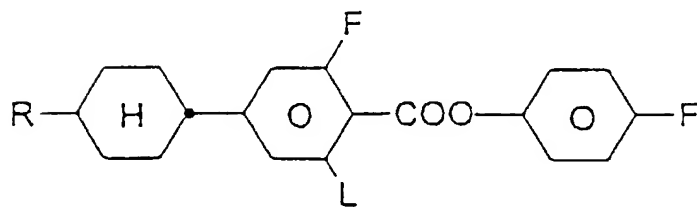
2. Phenol esters according to Claim 1, characterized  
 in that R is a straight-chain alkyl radical having  
 15 1 to 10 carbon atoms or an alkenyl radical having  
 2 to 10 carbon atoms.

3. Phenol esters according to Claim 1 or 2,  
 characterized in that

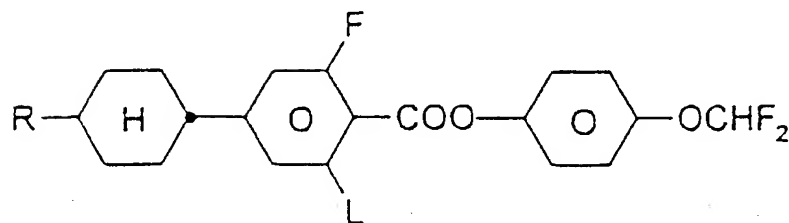
20 Y is F, Cl, CN,  $\text{CF}_3$ ,  $\text{CF}_2\text{H}$ ,  $\text{OCF}_3$ ,  $\text{OCF}_2\text{H}$ ,  $\text{OCFHCF}_3$ ,  
 $\text{OCFHCFH}_2$ ,  $\text{OCFHCF}_2\text{H}$ ,  $\text{OCF}_2\text{CH}_3$ ,  $\text{OCF}_2\text{CFH}_2$ ,  $\text{OCF}_2\text{CF}_2\text{H}$ ,  
 $\text{OCF}_2\text{CF}_2\text{CF}_2\text{H}$ ,  $\text{OCF}_2\text{CF}_2\text{CFH}_2$ ,  $\text{OCFHCF}_2\text{CF}_3$ ,  $\text{OCFHCF}_2\text{CF}_2\text{H}$ ,  
 $\text{OCF}_2\text{CF}_2\text{CF}_3$ ,  $\text{OCF}_2\text{CHF}_2\text{CF}_3$  or  $\text{OCClFCF}_2\text{CF}_3$ .

25 4 Phenol esters according to one of Claims 1 to 3,  
 characterized in that  $m = 1$ .

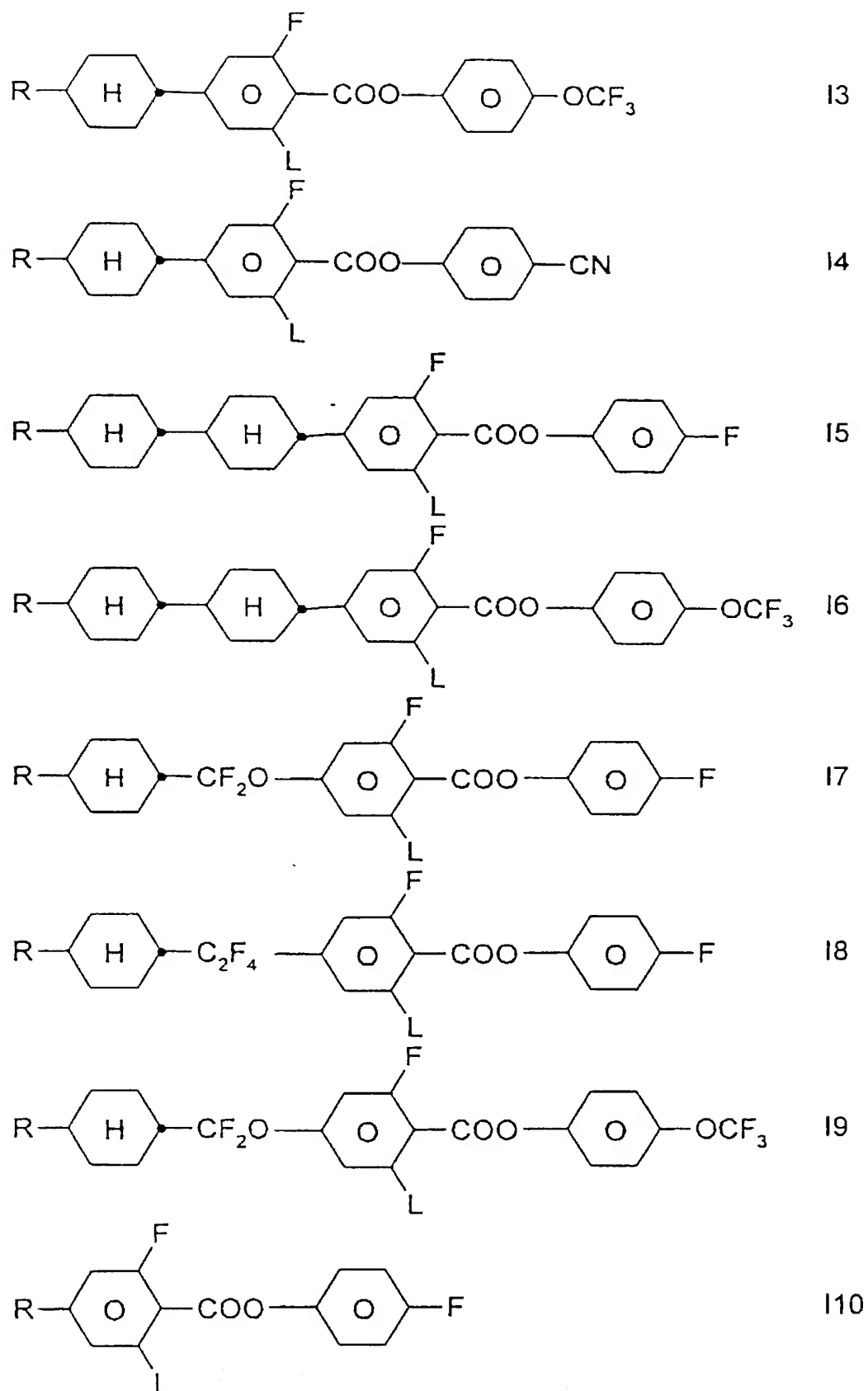
5. Phenol esters of the subformulae I1 to I12:



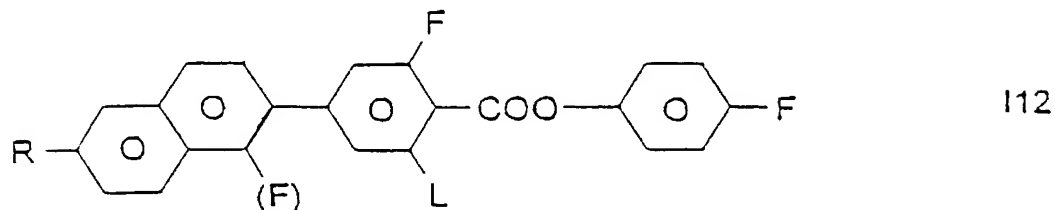
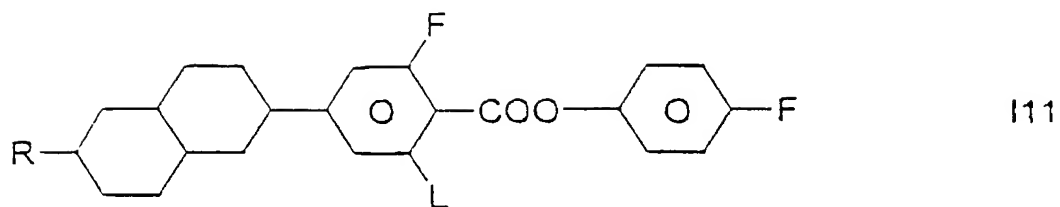
I1



I2



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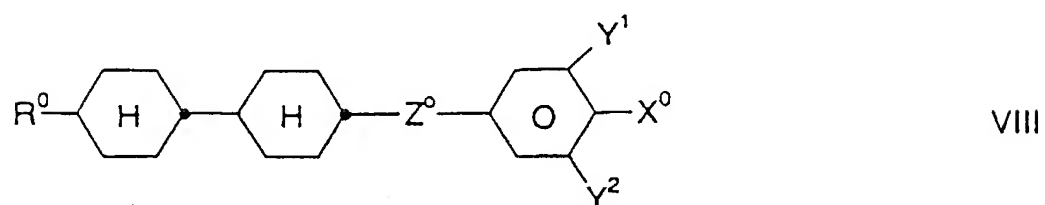
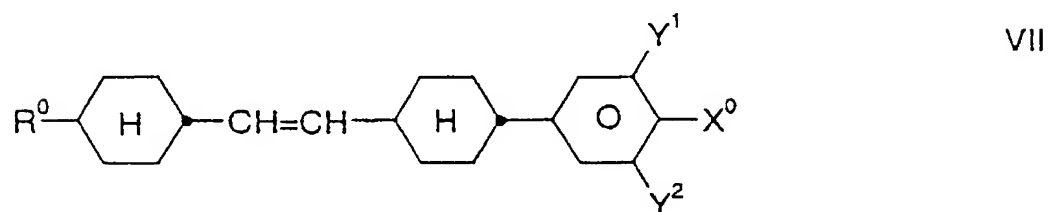
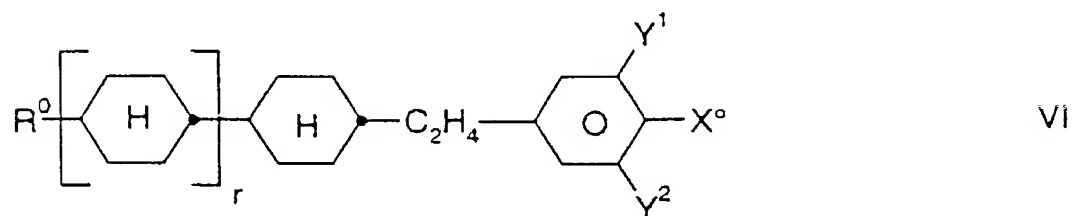
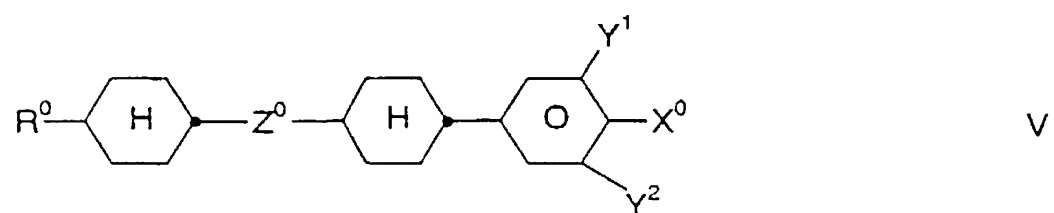
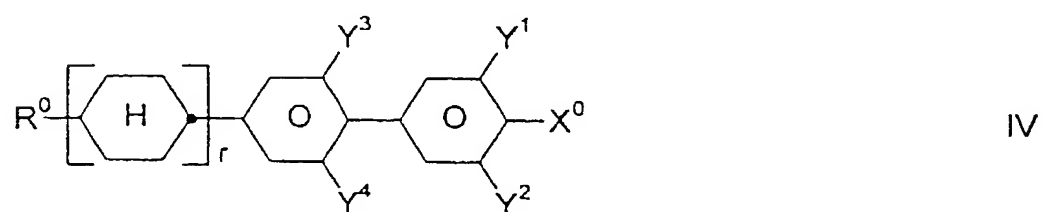
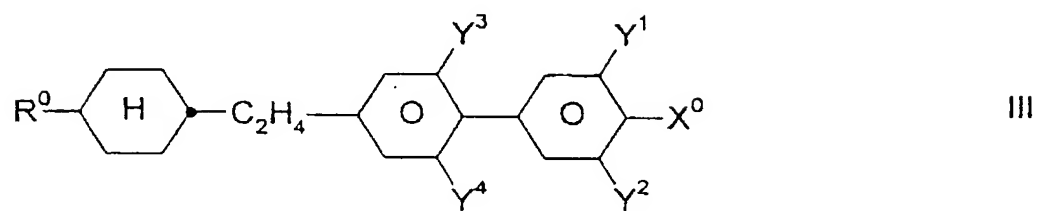
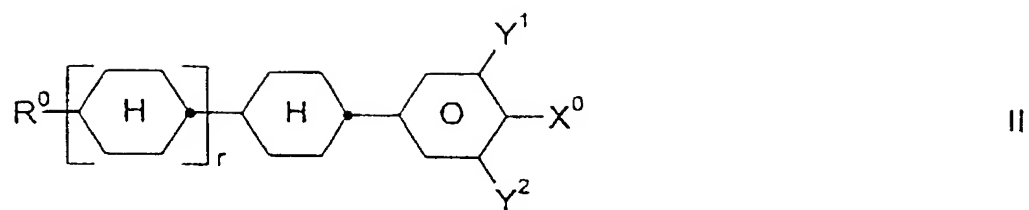
in which

R and L are as defined in Claim 1.

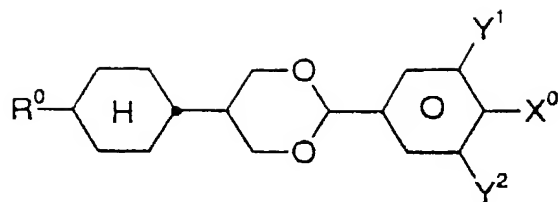
6. Liquid-crystalline medium comprising at least two mesogenic compounds, characterized in that it comprises at least one phenol ester according to Claim 1.
7. Liquid-crystalline medium according to Claim 6, characterized in that it additionally comprises one or more compounds selected from the group consisting of the general formulae II, III, IV, V, VI, VII, VIII and IX:



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IX

in which the individual radicals have the following meanings:

5

$R^0$  is n-alkyl, oxaalkyl, fluoroalkyl, alkenyloxy or alkenyl, in each case having up to 9 carbon atoms,

10

$X^0$  is F, Cl, halogenated alkyl, alkenyl or alkoxy having 1 to 6 carbon atoms,

$Z^0$  is  $-C_2H_4-$ ,  $-C_2F_4-$ ,  $-CF_2O-$ ,  $-OCF_2-$  or  $-COO-$ ,

15

$Y^1$ ,  $Y^2$ ,  $Y^3$  and  $Y^4$  are each, independently of one another, H or F, and

20

$r$  is 0 or 1.

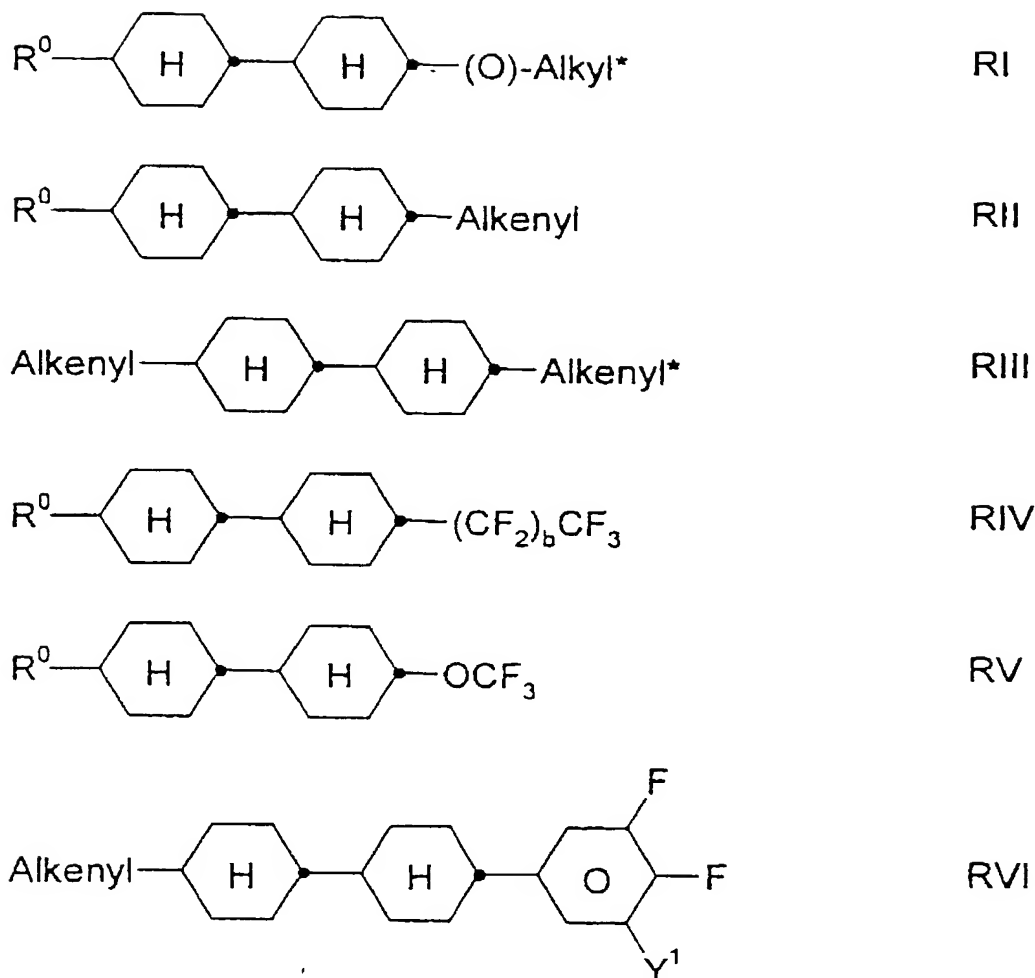
8. Medium according to Claim 6 or 7, characterized in that the proportion of compounds of the formulae I to IX in the total mixture is at least 50% by weight.

25

9. Medium according to one of Claims 6 to 8, characterized in that it additionally comprises one or more compounds of the formulae RI to RVI

30

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in which

5         $R^0$         is n-alkyl, oxoalkyl, fluoroalkyl, alkenyloxy or alkenyl, in each case having up to 9 carbon atoms,

10         $b$         is 0, 1 or 2,

15         $Y^1$         is H or F,

Alkyl\*    is a straight-chain alkyl radical having up to 9 carbon atoms,

Alkenyl or Alkenyl\*

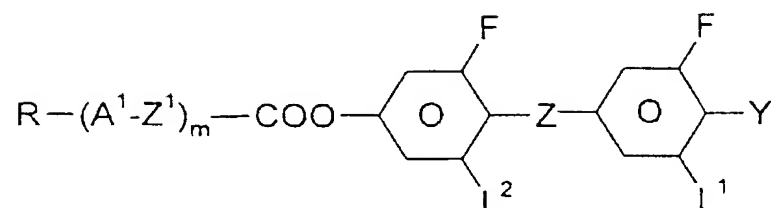
- 67 -

is, in each case independently of one another, an alkenyl radical having up to 9 carbon atoms.

- 5 10. Medium according to one of Claims 7 to 9, characterized in that  $X^0$  is F or  $OCF_3$  and  $Y^2$  is H or F.
- 10 11. Use of the liquid-crystalline medium according to Claim 6 for electro-optical purposes.
12. Electro-optical liquid-crystal display containing a liquid-crystalline medium according to Claim 6.

## Abstract

The invention relates to liquid-crystalline phenol esters of the formula I



in which

R, A<sup>1</sup>, Z<sup>1</sup>, m, L and Y are as defined in Claim 1, to liquid-crystalline media comprising at least one phenol ester of the formula I, and to electro-optical displays containing such a liquid-crystalline medium.

Docket No.  
Merck

## Declaration and Power of Attorney For Patent Application English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Liquid-crystalline phenol esters

the specification of which

(check one)



is attached hereto.



was filed on 18.09.2000 as United States Application No. or PCT International  
Application Number PCT/EP00/09133  
and was amended on \_\_\_\_\_

(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)

Priority Not Claimed

19947954.2  
(Number)

Germany  
(Country)

06.10.1999  
(Day/Month/Year Filed)



\_\_\_\_\_  
(Number)

\_\_\_\_\_  
(Country)

\_\_\_\_\_  
(Day/Month/Year Filed)



\_\_\_\_\_  
(Number)

\_\_\_\_\_  
(Country)

\_\_\_\_\_  
(Day/Month/Year Filed)



I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional application(s) listed below:

(Application Serial No.)	(Filing Date)

(Application Serial No.)	(Filing Date)

(Application Serial No.)	(Filing Date)

I hereby claim the benefit under 35 U.S.C. Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States of PCT International application in the manner provided by the first paragraph of 35 U.S.C. Section 112. I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, C.F.R., Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)

(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)

(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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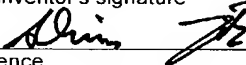
5 - 00

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